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CONTENTS

- L. H. KROL: "On the Occurrence of the Danauf ormation in Martapura (S. E. Borneo). (Communicated by Prof. L. RUTTEN), p. 338.
- W. H. KEESOM: "On the diffraction of Röntgen-rays in fused sodium and potassium", p. 341.
- F. FLORSCHÜTZ: "On a Dryasflora-bearing deposit in the Netherlands". (Communicated by Prof. L. RUTTEN), p. 344.
- P. ROGGEVEEN: "Profiles through the Synclines of Comblain au Pont and Chanxhe". (Communicated by Prof. L. RUTTEN), p. 346.
- J. H. DE BOER: "On Some Phenomena which are Caused by the Low Indices of Refraction of Alkali Boron Fluorides". (Communicated by Dr. G. HOLST), p. 350.
- S. GOUDSMIT: "The Structure of the Calcium Fluoride Band  $\lambda$  6087." (Communicated by Prof. P. ZEEMAN), p. 355.
- C. A. CROMMELIN and R. O. GIBSON: "The vapour pressures of solid and liquid neon". (Communicated by Prof. W. H. KEESOM), p. 362.
- J. H. DRUIF: "A contribution regarding the Mineralogical Composition of some of the Soils of the Netherlands". (Communicated by Prof. L. RUTTEN), p. 365.
- FRED. SCHUH: "Fusion of the existing Theories of the Irrational Number into a New Theory". (Communicated by Prof. D. J. KORTEWEG), p. 368.
- C. EYKMAN: "Experiments with JANSEN and DONATH's Antiberiberi-vitamin", p. 376. (With two plates).
- J. J. VAN LAAR: "On the Heats, resp. Pressures of Evaporation Sublimation and Melting, also in the Neighbourhood of the Absolute Zero, in Connection with NERNST's So-Called Heat Theorem". (On the Equation of State of Solid Substances, IV). (Conclusion). (Communicated by Prof. H. A. LORENTZ), p. 383.
- F. A. H. SCHREINEMAKERS: "Equilibria in systems, in which phases, separated by a semi-permeable membrane" XX, p. 401.
- TAN SIN HOK: "Discoasteridae Incertae Sedis". (Communicated by Prof. H. A. BROUWER), p. 411.
- H. ZWAARDEMAKER: "On some Properties of the Radiation-substances (with weak radiation)", p. 420.
- O. BOTTEMA: "The Definition of Euclidean Measure in the Projective Plane". (Communicated by Prof. W. VAN DER WOUDE), p. 423.
- W. HUREWICZ: "Ueber das Verhältnis separabler Räume zu kompakten Räumen". (Communicated by Prof. L. E. J. BROUWER), p. 425.
- LAURETTA BENDER: "An Experimental Study of the Cerebellar Control of the Vocal Organs". (Communicated by Prof. G. VAN RIJNBEEK), p. 431.
- Erratum, p. 440.

**Geology.** — *On the Occurrence of the Danauf ormation in Martapura (S. E. Borneo).* By L. H. KROL. (Communicated by Prof. L. RUTTEN).

(Communicated at the meeting of October 30, 1926).

Dr. J. K. VAN GELDER kindly sent me an off-print of the Proceedings of the "Koninklijke Akademie van Wetenschappen" at Amsterdam (Section for Physics), containing a communication by Prof. L. RUTTEN on the subject expressed in the title of this paper. As I do not get off with a whole skin there, I may be allowed to put in a rejoinder.

First of all I must premise that I am now isolated in the "rimbu" of W. Borneo and secluded from all the literature and maps, so that I feel somewhat handicapped in my defence. Still, I will try to call to mind the material that has to back me up.

When residing in the Southern- and Eastern Division I often asked myself how HOOZE came to speak of Alino- and Waringin *clayrock*. Whenever I crossed this formation, I was confronted especially with siliceous rocks with very fine-grained weathering products.

I grant that some hand-specimens he broke off are indeed *clayrocks*, although the qualification "sticking to the tongue" cannot serve as the only criterion for the determination. Now it appears that of the 19 rocks determined more precisely by Prof. RUTTEN, no fewer than 14 are called *siliceous slate*, *silicified tuff* or *siliceous*.

By using the term *clayrock* HOOZE has caused confusion, and has led his successors somewhat astray.

For the present demonstration I start from the position of the Intrusiva of Martapura in the geological profile. At the time I came to the conviction that these rocks (namely in the Meratus mountains) are intracenomanian, because they have metamorphosed, especially along the south, the cenomanian limes with *Orbitulina concava* into marble, where-with also magnetite originated (see KROL Jb. Mijnwezen 1918. Proceedings p. 330 and Verslagen en mededeelingen betreffende Indische Mineralen en hunne Toepassing N<sup>o</sup>. 9 — IJzererts en van Pleihari).

It might be argued that only in one locality, viz. near the Batu Kora, both the contact phenomenon, and the presence of *Orbitulina* have been recognized, which would go against my conception by assuming, e.g. that the intrusiva of the Meratus mountains are older than Cenomanian and that this intrusiva rock of the Batu Kora is the only one that is intracenomanian.

But if we mark all the localities of these iron-ores on the map from Talok-Takisung on sea in the south-west, as far as the Sei Pontain in



the north east, it will be seen that all these localities are situated on three parallel lines, which tectonic lines run again parallel to those of the Meratus-mountains. The limes have disappeared almost everywhere, and have fallen a victim to erosion. Only a few relics are extant of the vast and stupendous lime-rocks of olden time.

This, in my opinion, is sufficient proof of contact-metamorphous activity of the intrusiva during the Cenomanian over their whole length, so I wonder that Prof. RUTTEN has taken so little notice of my account, and calls my conclusions singular.

In those places where the lime has been destroyed by erosion, the iron-ore (assuming a vertical descent) lies on the rock on which the lime has been built up. I assume a vertical descent, not a rolling displacement because nearly all the iron-ores are situated on the tops of the hills (e.g. G. Tembaga near Pleihari). On that account these rocks are older than the Orbitulina-limes, but since they are also metamorphous, I take them to be the lowest layer of the Cenomanian.

Macroscopically and microscopically these rocks are quite similar to the Tambam-quartzites, already found by VERBEEK, for which reason they are referred by me to the Cenomanian. But when looked at they also resemble the rocks of G. Waringen.

Most often they are grey with pink tints and black veins, they have a very irregular cleavage, which reminds us of pressure phenomena, but the usual microscopic inspection did not reveal radiolaria<sup>1)</sup>.

Since I did not consider it probable that the mighty intrusiva should have generated contact-phenomena only on the south side, I supposed them to have occurred also on the north side. In the Meratus-mountains the crystalline rocks received consideration in this respect (see KROL p. 330 1<sup>st</sup> paragraph); in the Bobaris-mountains in the centre the crystalline slates; in the north the Alino- and Waringin-layers.

That these rocks are metamorphous, is also evident from the description by HOOZE and RETGERS.

Besides it is also apparent from the picture of the landscape, I admit, however, that also older rocks may have been metamorphosed by the intracenanomanian intrusiva. (See l. c. p. 331).

Now Prof. RUTTEN has been confronted with radiolaria in the Waringin-Alino-rocks, which he parallels with the Danauf ormation of MOLENGRAAFF in W. Borneo. Whether this is quite admissible over such a distance, I will leave undecided here; no doubt a closer palaeontological examination — such as HINDE's examination of MOLENGRAAFF's radiolaria — could certainly have yielded more positive evidence.

I take it, however, that similar stupendous movements of the soil have

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<sup>1)</sup> During my geol. survey of the Paloh-district I found on Gg. Rasau (Serawak boundary) quite similar rocks, which on microscopical examination by Dr. GISOLF appeared to contain radiolaria and are on that account referred by me to the Danauf ormation.

not taken place within comparatively narrow limits, so that I shall have to revise my opinion about that part of Borneo.

Then, however, the consequence of RUTTEN's find is that this Danauf ormation will appear to occur over a very large tract in the part of Borneo mapped by HOOZE and myself, so that the major part of what I marked as Cenomanian has to be considered as Trias-Jura. (See KROL p. 354 bottom).

To sum up we come to the following conclusion:

1<sup>o</sup>. The intrusiva of the Bobaris and Meratus-mountains are to be considered provisionally as intracenanomanian, until other data shall be known.

2<sup>o</sup>. These intrusiva have metamorphosed the sediments of the Cenomanian as well as those of the Danauf ormation.

In conclusion Prof. RUTTEN's find opens up singular perspectives relating to the origin and the locality of the Borneo-diamonds. The data, however, have not yet been sufficiently studied for further communications.

*Ngabang-Landak, July 1926.*

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**Physics.** — *On the diffraction of Röntgen-rays in fused sodium and potassium.* By Prof. W. H. KEESOM. (Supplement No. 61a to the Communications from the Physical Laboratory at Leiden).

(Communicated at the meeting of December 18, 1926).

§ 1. *Introduction.* The communication of PRINS <sup>1)</sup> about the diffraction of Röntgen-rays in mercury acted as an inducement to me to publish the results of a similar investigation about sodium and potassium in the fused state. This piece of research was carried out by me in 1923 in the Laboratory of Physics and Physical Chemistry of the Veterinary College as a part of an investigation on the diffraction of Röntgen-rays in solutions of liquid-mixtures <sup>2)</sup>. The latter however has not been continued because of my departure to Leiden <sup>3)</sup>.

§ 2. *Method.* The fused metal to be radiated, was brought into a thinwalled glass tube, in vacuo, in order to prevent as far as possible the inevitable formation of oxide. This tube was put into the middle of a DEBIJE—SCHERRER-camera, as described in Comm. N<sup>o</sup>. 10 from the Laboratory of Physics and Physical Chemistry of the Veterinary College <sup>4)</sup>. The lower part of the tube was immersed in a small beaker-glass filled with paraffine, which was kept, by means of an electrically heated resistance wire, at a temperature of about 25 degrees above the melting point of the metals (controlled with the aid of a thermoelement, brought into the paraffine). Separately we had made sure that then the whole mass of the metal present was molten. The metal was radiated (Cu-K-rays) some few millimeters above the part immersed in the paraffine. For K we worked with a HADDING tube for 23 hours with 22 mA; for Na 7<sup>1</sup>/<sub>2</sub> hours with 17 mA.

§ 3. *Results.* The results obtained are given in table I. Here  $\varphi$

TABLE I.

Sub- stance	Diameter diffractionring	$\varphi$	$\varphi_{corr.}$	$a$	$\delta$	$1.33 \sqrt{\frac{M}{\delta}}$
Na	27 mm.	28.6°	27.1°	4.04 Å	0.93 <sup>5)</sup>	3.88 Å
K	21.5 „	22.8	21.2	5.13	0.83 <sup>5)</sup>	4.80

<sup>1)</sup> J. A. PRINS. *Physica* 6, 315, 1926.

<sup>2)</sup> Some data about this are communicated in § 5.

<sup>3)</sup> This investigation was already mentioned in Comm. Leiden, Suppl. N<sup>o</sup>. 53b, 1924, p. 17, note 2.

<sup>4)</sup> W. H. KEESOM and J. DE SMEDT, *These Proc.* 25, 118.

<sup>5)</sup> VICENTINI and OMODEI 1888.



represents the half top angle of the cone formed by the diffracted Röntgen-rays, as this is found from the half diameter of the diffraction ring on the film and the radius of the cylinder inside which the film has been bent (27 mm). In  $\varphi_{\text{corr.}}$  the correction for the thickness of the cylinder of molten metal (the tube had a diameter of 1.1 to 1.2 mm) has been applied after BIJL and KOLKMEIJER <sup>1)</sup>,  $a$  is the distance of the diffracting particles, calculated after the formula of EHRENFEST <sup>2)</sup>:  $a = 7.72 \lambda / 4 \pi \sin \frac{\varphi}{2}$ ;  $\delta$  is the density of the liquid. The last column gives the distance of two neighbouring atoms, assuming that these are packed as closely as possible in the volume occupied by the liquid <sup>3)</sup>.

§ 4. In the first place it appears from the approximating agreement of columns 5 and 7 of table I, that, just as in the cases of the liquids mentioned in the Communications N<sup>o</sup>. 10 and 12 from the Laboratory of Physics and Physical Chemistry of the Veterinary College <sup>4)</sup>, also with Na and K the distance of each two diffracting particles agrees approximately with the distance of two neighbouring particles, arranged in closest packing; the distance of two diffracting particles being derived from the diameter of the diffraction rings with the formula of EHRENFEST.

As in my calculations for Na and K the atomic weight is taken for  $M$ , it follows that these elements, just as A and Hg, are monatomic liquids.

It is interesting to note that the two numbers of column 7 are smaller than the corresponding ones of column 5, and although the difference is hardly beyond the limits of experimental error, it is perhaps significant that the same is found in the case of argon when one applies the correction of BIJL and KOLKMEIJER to the observations of Comm. N<sup>o</sup>. 10 l.c. <sup>5)</sup> as is shown in the following table.

TABLE II.

Sub- stance	Film N <sup>o</sup> .	Diameter diffractionring	$\varphi$	Diameter preparation	$\varphi_{\text{corr.}}$	$a$	$1.33 \sqrt[3]{\frac{M}{\delta}}$
A	37	26.75	28.4°	3.0 mm.	23.7°	4.61 Å	4.08
..	53	25.5	27.0	2.0 ..	24.0	4.55	4.08

<sup>1)</sup> A. J. BIJL and N. H. KOLKMEIJER, Comm. N<sup>o</sup>. 2a from the Laboratory of Physics and Physical Chemistry of the Veterinary College; These Proc. **21**, 496, note 1; A. J. BIJL, Thesis for the Doctorate, Utrecht 1918.

<sup>2)</sup> P. EHRENFEST, These Proc. **17**, 1184.

<sup>3)</sup> Compare W. H. KEESOM and J. DE SMEDT, Comm. N<sup>o</sup>. 10, l.c.

<sup>4)</sup> These Proc. **25**, 118 and **26**, 112.

<sup>5)</sup> For the other substances investigated there, which show a much smaller absorption-power for the Röntgen-rays, this correction will be much less.

That difference can be partly ascribed to the influence (comparatively larger for argon than for sodium and potassium) of the dimensions of the atom (comp. § 5 of the mentioned Comm. N<sup>o</sup>. 10) but probably not completely.

§ 5. Though I will not connect conclusions with this, I may utilize the opportunity to communicate the results of another two Röntgenograms, namely those of a solution of NaCl in water, and of a mixture of water and aethylalcohol. The following table gives the half top angle of the cone formed by the diffracted Röntgen-rays for Cu-K-rays, with the liquids mentioned. To it are added the relative values for water and aethylalcohol as previously obtained (Comm. N<sup>o</sup>. 10 l.c.)

water	$\varphi = 29^\circ$ , further blackening to $\varphi = 46^\circ$
alcohol	$22^\circ$ , " " " " $\pm 43.5^\circ$ (limits
30 gr. NaCl + 100 gr. H <sub>2</sub> O	$31^\circ$ unclear)
18 gr. H <sub>2</sub> O + 46 gr. C <sub>2</sub> H <sub>6</sub> O	$23^\circ$ , second ring $42^\circ$ .

The ring of NaCl was (because of insufficient exposure) weak, but still clear; the film of the water-alcohol-mixture showed an intensive ring (extending itself from  $\varphi = 20^\circ$  to  $\varphi = 26^\circ$ ). Within and outside the ring there was a weak blackening, the last ending into a weak second ring at  $\varphi = 42^\circ$ .

**Palaeontology.** — *On a Dryasflora-bearing deposit in the Netherlands.*  
By F. FLORSCHÜTZ. (Communicated by Prof. L. RUTTEN).

(Communicated at the meeting of January 29, 1927).

In 1891 the Swedish palaeobotanist A. G. NATHORST summarized his experiences about the occurrence of fossil remains of arctic plants within the area of the former North-European icesheet as follows:

"Bevor ich Norddeutschland verlasse, muss ausdrücklich betont werden, dass die arktischen Pflanzenreste in einer ganz bestimmten glacialen Süßwasserformation hier vorkommen. Diese Formation findet sich über die ganze Moränenlandschaft Norddeutschlands und Westrusslands verbreitet (ganz wie in Schonen und Dänemark) und man kann folglich dort die Zahl der Fundstätten nach Belieben vermehren" <sup>1)</sup>.

The said "Formation" forms part of a complex of layers always resting upon the moraine and consisting in descending sequence of peat, "gytja", peatlime and freshwater-clay and -sand of which either the "gytja" or the peatlime or both may be wanting. According to this author only *Betula nana* L. sometimes occurs in the peat; for the rest the remains of arctic plants are confined to the "gytja", the peatlime, the clay and the sand, especially to the last-mentioned two sediments <sup>2)</sup>.

Directed by this information I went in search of fossil arctic plants in the Netherlands. First of all my attention was drawn to the spots where peatlime occurs at a short distance from boulderclay, as it is possible that the moraine extends under the lime.

Two places, one near Markelo in the province of Overijssel and the other south-west of Winterswijk, were chosen for further investigation.

An inundation in the last months of 1926 provisionally eliminated the marshes of Markelo. I therefore first confined myself to the bog of Blekkink in the vicinity of Winterswijk.

VAN BAREN records lime under peat on that spot <sup>3)</sup>.

On the 28<sup>th</sup> of December 1926 a profile was dug near a brook intersecting the field. From the top downwards the following order was to be observed: surface soil 10 cm.; sandy loam 20 cm.; peat 30 cm.; peatlime 35 cm.; clay 30 cm.; grey sand 50 cm.

The floor of the sand was not reached at that time neither when

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<sup>1)</sup> Ueber den gegenwärtigen Standpunkt unserer Kenntnis von dem Vorkommen fossiler Glacialpflanzen. Bihang till Kongl. Svenska Vetenskaps-Akademiens Handlingar. Band 17 Afd. III. N<sup>o</sup>. 5. p. 20.

<sup>2)</sup> Loco citato p. 5, 6 and 7.

<sup>3)</sup> De bodem van Nederland, p. 716.



further efforts were made especially owing to the high level of the groundwater and the insufficient boring-apparatus. The presumption that under the sand boulderclay is to be found, as in places quite near it rises to the surface, could therefore not be confirmed at that time.

On examining the collected material a topfragment of a leaf of *Dryas octopetala* L. was found in the layer forming the transition from peatlime to clay.

A further investigation of this sediment consisting partly of lime partly of clay yielded a great many endocarps of *Potamogeton*, some seeds of *Myriophyllum spicatum* L. and of *Betula* (probably not of *Betula nana* L.), many epidermisfragments of *Phragmites*, multitudinous *Chara-oogonia*, *Diatomeae*, insects-rests, shells of *Ostracoda* and freshwatermolluscs.

Considering the following facts I may presume here a findingplace of the so-called *Dryasflora*.

NATHORST records as parts of this former vegetation besides *Dryas octopetala* L. especially the waterplants *Myriophyllum* and *Potamogeton* <sup>1)</sup>. Moreover he reports the occurrence of the following typical fauna accompanying the arctic plantrests: some *Pisidia*, *Anodonta* or *Unio*, *Limnaea ovata* and *Cyclas cornea* <sup>2)</sup>.

VAN BAREN gives an enumeration of the shells found in the peatlime of Blekkink-bog, including some *Pisidia*, *Limnaea ovata* and *Sphaerium corneum* (syn. *Cyclas cornea*) according to the determination of M. SCHEPMAN <sup>3)</sup>.

The review of the organic rests found in the "Dryashorizont" of North-Germany, given by PAUL RANGE, contains *Betulae* (also other ones besides *Betula nana* L.), *Phragmites* and *Charae*, and among the zoological remains *Ostracoda* <sup>4)</sup>.

Besides the nature and order of the layers of the profile correspond with the general scheme composed by NATHORST.

The site of Blekkinkbog is about 40 m. above sealevel, 51° 55' N. and 6° 40' E. of Greenwich.

I am greatly indebted to Dr. A. TH. TEN HOUTEN and Docts. G. VAN EEKELEN of Winterswijk and to Mr. W. KRUISELBRINK, agriculturist on Blekkinkhof, for their kind assistance during the exploration of the field.

*Velp (G.), Holland, January 10<sup>th</sup> 1927.*

<sup>1)</sup> Loco citato p. 12.

<sup>2)</sup> " " p. 7.

<sup>3)</sup> " " p. 716.

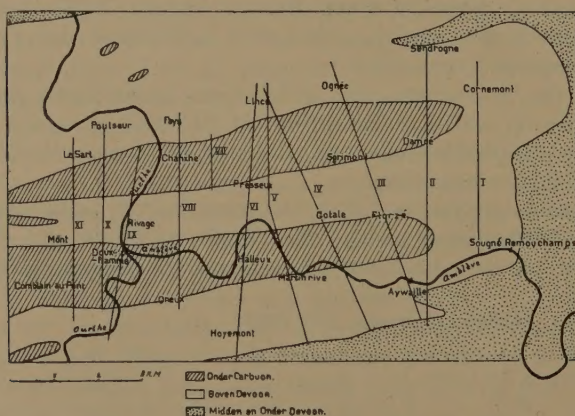
<sup>4)</sup> Das Diluvialgebiet von Lübeck und seine Dryastone. Zeitschrift f. Naturwiss. Bd. 76. 1903. p. 232—241.

**Geology.** — *Profiles through the Synclines of Comblain au Pont and Chanxhe.* By P. ROGGEVEEN. (Communicated by Prof. L. RUTTEN).

(Communicated at the meeting of January 29, 1927).

Our knowledge of the structure of the region of the synclines of Comblain au Pont and Chanxhe, constituting the most eastern part of the Carbonian basin of Dinant, is still limited. An exception is afforded by the Ourthe-profile, which has already been described and mapped by LOHEST and FORIR<sup>1)</sup>. We deemed it well worth consideration to give a description of these synclines, as it would add to our knowledge of a portion of the Belgian Ardennes, situated at a rather short distance to the south of the so-called "Faille Eifeliennne". According to FOURMARIER and to most of the other Belgian geologists this is to be considered together with the "Faille du Midi", as the northern limit of an important overthrust-sheet, so that the region under consideration will probably belong to it.

The body of facts collected last summer in the well-exposed territory, enabled us to reconstruct a number of profiles through the synclines. The accompanying map gives a survey of the territory we examined.



Onder Carbon = Lower Carboniferous  
 Boven Devoon = Upper Devonian  
 Midden en Onder Devoon = Middle- and Lower Devonian

The location of the profiles is indicated by the lines I—IX. The

<sup>1)</sup> Annales de la Société Géologique de Belgique, tome 22, 1894/95.

statigraphical division in the profiles is the same as that of the Belgian geological map 1 : 40.000, though the stratigraphy that has been adopted in recent times, slightly departs from it. This, however, matters little for the description of the tectonic.

In our survey we adopted the subdivision of the Belgian geological map for the more detailed observations, as regards the Upper-Famennien; as regards the lower-Carbonian we used the subdivision given by LOHEST<sup>1)</sup>.

The trend of the profiles is on the whole N.—S., which is normal to the general strike. The profiles have been orientated by giving the names of the places and the azimuth. The situation of the profiles I, II and VII, however, could not be indicated out with sufficient accuracy in this way. A few items concerning them may follow: At A in profile I point is a marked 750 m. west of Amblève-bridge at Sougné-Remouchamps. Point B in profile II is 375 m. east of Amblève-bridge at Aywaille. Point C in profile VII lies 1180 m. east of Ourthe-bridge at Chanxhe.

Profile IX, reconstructed from personal observations, corresponds with the Ourthe-profile, as given by LOHEST and FORIR.

Localities, where complications appeared, which could not be explained, because of the too small number of observations, occurred: first, to the south of profile I, so that the reconstruction of this profile was discontinued; secondly, in profile X and XI in the syncline of Chanxhe and the adjacent anticline to the South.

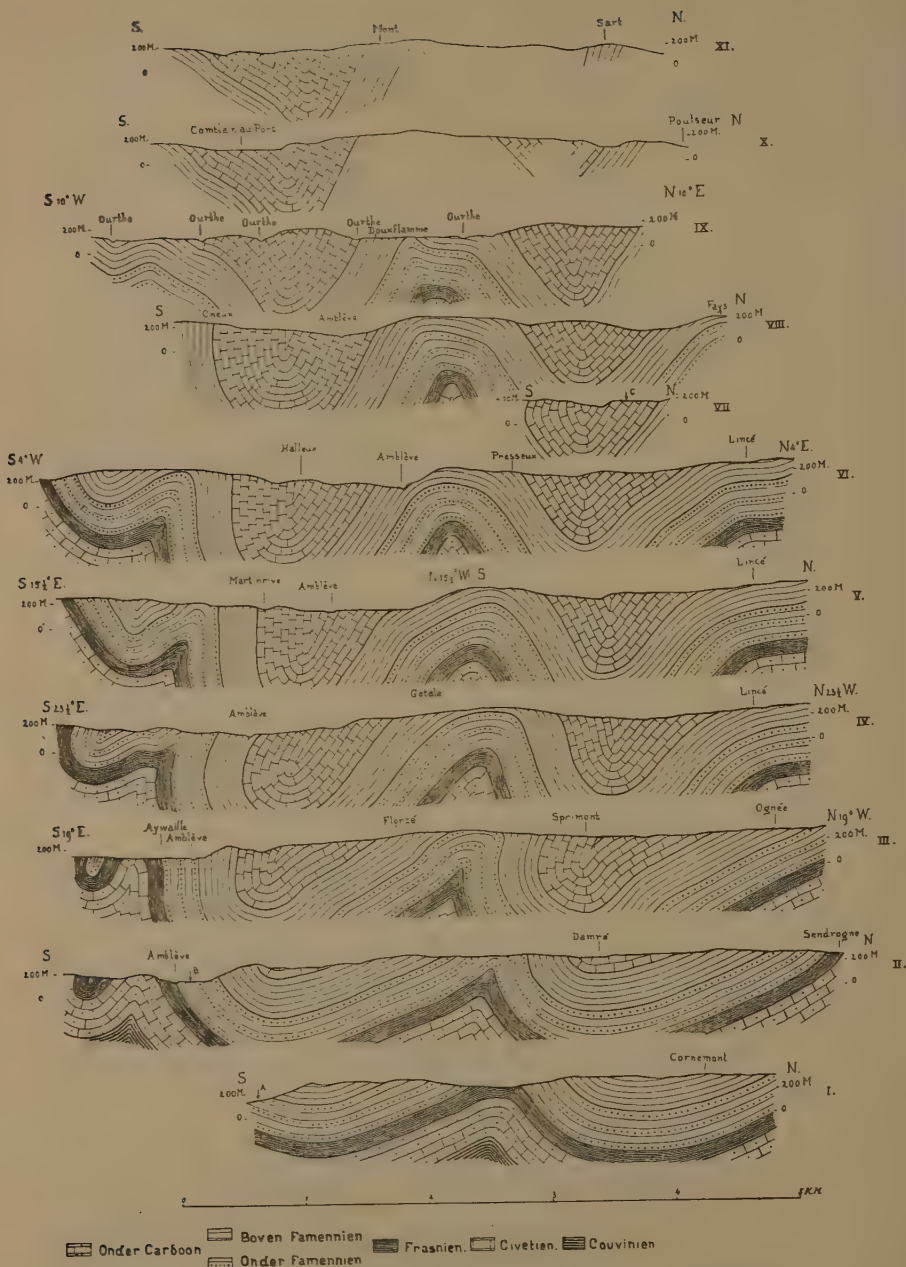
Departures from the Belgian geological map were rarely met with. One instance is that in profile I — in the anticlinal nucleus south of Cornemont — Frasnien still crops out over a distance of certainly not less than 300 m., whereas the map indicates only Lower-Famennien. Probably the map is not correct either with respect to the localities, where the above-named complications occurred.

The eastern profiles represent the commencement of the two synclines. When the *Syncline of Comblain* becomes deeper, it soon presents a steep Southern-limb, which is in Profile III slightly overturned Northward. In Profile IV this overturning is more pronounced (a.o. 60° S. in the Southern-limb). Farther to the West the Southern-limb remains very steep, while the Northern-limb everywhere shows smaller dips than the Southern-limb. In the Ourthe-profile (IX) it is the other way about: there the Northern-limb is steeper than the Southern-limb, which is also the case in profiles X and XI.

In the east the *Syncline of Chanxhe* shows also in the Southern-limb larger dips than in the Northern-wing. Here such an asymmetry reveals itself, as is seen in the eastern portion of the syncline of Comblain au Pont: in profile II the Southern-limb is inappreciably overturned; in

<sup>1)</sup> LOHEST: Les facies du Dinantien, 2me partie: Régions orientales de la Belgique. Livret Guide du Congrès Géologique International, 1922, Excursion C3.





Onder Carboon = Lower Carboniferous

Boven Famennien = Upper Famennian

Onder Famennien = Lower Famennian

Frasnien = Frasnian   Givetien = Givetian   Couvinien = Couvinian

profile III this overturning is more pronounced (dips of e.g.  $70^{\circ}$  S.). To the West of it the syncline yields more symmetrical sections, except in profile VII, where the South-limb dips locally to the South.

In the eastern profiles the anticline, lying between the two synclines, has larger dips in the Northern-wing than in the Southern. In profile VI it yields an approximately symmetrical section. More to the West the top gets flatter and at the Ourthe it sags. This proceeds probably more Westward into a small *Carboniferous* syncline.

The profiles II, III, IV, V, VI, and IX, which have been extended farther south than the others, represent sections of a syncline beginning in the east. There the Southern-limb dips southward (profile II, III, and IV).

To the west of this the syncline soon gets more normal, broader, and deeper.

The anticline between this syncline and that of Comblain au Port lays bare the Givetien in profile II and III. Then, however, it soon sinks rather rapidly and has subsided so deep in profile IX, that it forms only a feeble severance between the two synclines.

In fine it appeared from the profiles that the Frasnien and the Lower Famennien in the Southwest is considerably thinner than in the East and the North-east.

Nowhere, except in localities where the above-stated complications occurred, did we find any indication of faulting in the tectonic. We were invariably encountered with a normal sequence of subdivisions.

It strikes us that this territory which probably belongs to the overthrust-sheet, presents no faults of any significance, either longitudinal or transversal ones.

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**Physics.** — *On Some Phenomena which are Caused by the Low Indices of Refraction of Alkali Boron Fluorides.* By J. H. DE BOER.  
(Communicated by Dr. G. HOLST).

(Communicated at the meeting of February 26, 1927).

In the preparation of simple or complex fluorides it may often occur that already a considerable quantity of salt has crystallised or has been formed as a precipitate, the latter not being visible. The explanation is simply that the indices of refraction of most fluorides are so low that they are in the neighbourhood of their saturated solutions. The boundaries of separate crystals are consequently difficult to distinguish; powdery precipitates become transparent.

These phenomena were particularly marked in the preparation of the alkali boron fluorides. When the sparingly soluble potassium salt is precipitated by double transformation of boron fluor hydrogenic acid,  $\text{HBF}_4$ , with a solution of potassium chloride, it is possible that the precipitate is hardly visible. It is stated in the literature that the salt is deposited as a gelatin, which does not pass into a crystalline form until later. The precipitate is, however, only apparently a gelatin; this is perceived when the salt is sucked off. The filtration proceeds exceedingly rapidly; as long as the mass is still wet, it is quite transparent; as soon however as the upmost layer of the salt is sucked dry, the filter is suddenly seen to be quite filled with a white crystalline substance.

Now the indices of refraction of the alkali boron fluorides are very low indeed, which was clearly demonstrated in the preparation of the cesium salt,  $\text{CsBF}_4$ . A precipitate of the cesium salt, obtained by double transformation of a solution of  $\text{HBF}_4$  (from fluor hydrogenic acid and boric acid) with cesiumchloride, was not only perfectly transparent, but displayed besides brilliant colour effects. In a definite solution, in which cesium salt was precipitated, green light was e.g. perfectly transmitted, the other colours being still more or less dispersed in the precipitate. Objects, viewed through the precipitate, were therefore coloured green, being surrounded by a red-violet border. The index of refraction of the cesium salt<sup>1)</sup> is, therefore, so low that in the green it is equal to that of the above solution containing hydrochloric acid, the colour effects being caused by the difference in dispersion between salt and solution.

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<sup>1)</sup> The alkali boron fluorides are orthorhombic, hence they have, strictly speaking, three indices of refraction. This, however, is disregarded, and by index of refraction of the salt only a mean value is meant.



We find here a phenomenon analogous to that in potassium silico fluoride,  $K_2SiF_6$  <sup>1)</sup>, of which BERZELIUS already states that during the precipitation rainbow colours are visible, and that the salt is deposited as a gelatin through which colours play.

The dispersion curve of the cesium boron fluoride has a less steep course than that of the solution, which is clear from the fact that by careful dilution of the solution or by gentle heating the colour of the transmitted light changed from green to blue, the dispersed colours changing from red-violet to brownish yellow.

The index of refraction of the above solution at 20° C. for the D-line appeared to be: 1.3502. Hence the "index of refraction" of  $CsBF_4$  for the D-line lies somewhat higher than this value.

In another solution, in which the initial substances were brought together in more concentrated form, orange light was transmitted, the scattered light being greenish blue. The index of refraction of  $CsBF_4$  for the D-line is, therefore, slightly *smaller* than the index of refraction for the D-line of this latter solution, which appeared to be 1.3563. Hence we know now:

$$1.3563 > n_D \text{ for } CsBF_4 > 1.3502.$$

This low value for the index of refraction of  $CsBF_4$  might have been predicted on the ground of FAJANS and JOOS' considerations <sup>2)</sup>. By the aid of definite suppositions as to the deformation of the electron layers in ions these investigators have succeeded in constructing a table of refractions for the ions, the latter being supposed as gaseous and undeformed. Thus they give as value for the triply charged boron ion 0.05, for the singly negatively charged fluor ion 2.5. Now in  $(BF_4)'$  the boron ion will give the same value, the deformation under the influence of the fluor being only small. The fluor ions themselves are, however, strongly onesidedly deformed by the boron ion; their value of refraction is greatly lowered. We can, however, approximately evaluate how great this diminution is. While the free chlorine ion has a refraction 9.0, this value is diminished to 6.97 in  $BCl_3$ , i.e. to 77 % of the original value. Likewise the free bromine ion has a value of 12.67, in  $BBr_3$  9.97, hence only 79 %. Therefore we might say that in the neutral  $BF_3$  the fluor had decreased to about 75 % of its value, and amounts therefore to 1.9. In the  $(BF_4)'$  the deformation of the fluor ion will again be somewhat smaller, so that the value there will be  $> 1.9$ . Hence we get a refraction  $> 7.65$  for the  $(BF_4)'$ .

The free  $Cs^+$  has a refraction 6.24. Contrary to many other salts we may assume that in  $CsBF_4$  the ions influence each other only to a small extent. For the  $(BF_4)'$  is little deformable (like  $ClO_4'$ , an example which FAJANS and JOOS cite), and  $Cs^+$  is little deforming; also the reverse, i.e.

<sup>1)</sup> This is fully described by R. W. WOOD, Physical Optics 1921, p. 112.

<sup>2)</sup> K. FAJANS and G. JOOS. Zeitschr. f. Phys. **23**, 1, 1924.

a deformation of  $\text{Cs}'$  by  $(\text{BF}_4)'$  can practically be excluded. We therefore arrive at the conclusion that the refraction of  $\text{CsBF}_4$  has a value  $> 7.65 + 6.24$ , hence  $> 13.89$ .

As therefore

$$\frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d} > 13.89$$

it is only necessary to know the density  $d$  to arrive at a valuation of  $n$ . The density proved to be 3.2, hence we find for the index of refraction:

$$n_D > 1.33.$$

On the ground of such considerations it would be expected that the indices of refraction of rubidium and potassium boron fluoride are still lower. We shall see that this is actually the case.

While the appearance of the colour effects in the precipitation of the cesium salt is more or less accidental (because the dispersion curve intersects that of the mother liquid which contains hydrochloric acid) the matter is simpler in the rubidium boron fluoride.

During the precipitation no colour effects are observed, evidently because the index of refraction lies lower than that of the solution. In the recrystallisation of  $\text{RbBF}_4$  from pure water brilliant colours make their appearance. A solution of  $\text{RbBF}_4$  saturated at room temperature (0.6 gr. in 100 cc.) appears to have the same index of refraction as pure water (1.3332). If solid  $\text{RbBF}_4$  is brought into this solution, it again looks gelatinous; it appears that the yellow light is transmitted and that the dispersed colours cause blue borders. The index of refraction of  $\text{RbBF}_4$  for the D-line appears, therefore, to be very near 1.33 indeed.

In  $\text{CsBF}_4$  the play of colours could be varied at pleasure on dilution with water or on addition of  $\text{HCl}$  (on dilution of a very concentrated  $\text{HCl}$ -solution, which contained  $\text{CsBF}_4$  and transmitted *red* light, we could pass through the whole spectrum, the complementary colour always appearing as border colour round the objects); this did, of course, not succeed in the case of rubidium salt. It is still possible to vary the colour, namely by heating the system; the indices of refraction of the solution diminish more rapidly than those of the salt, so that at higher temperatures the points of intersection of the curves shift more towards the violet.

It may be seen from the following table that in this salt really pretty well the whole spectrum can be traversed in this way.

The index of refraction of potassium boron fluoride lies still lower than that of the rubidium salt, hence also lower than that of water. A solution of the potassium salt saturated at room temperature (only 0.6 gr. in 100 cc.) had again practically the same index of refraction as that of water. The solid salt brought in this solution displays hardly any colours. Only a blue dispersion is very faintly perceptible; also the separation

between salt and solution is much clearer. Evidently the dispersion curve of the potassium salt does not intersect that of water, but it lies under

$\text{RbBF}_4$  in water

Temperature	Colours of the transmitted light	Colours of the dispersed light
0°	orange	green-blue
10°	orange yellow	blue
20°	yellow	blue
30°	green yellow	blue violet
40°	yellow green	violet with some red
50°	yellow green	faint red violet
55°	green	red violet
60°	green with some blue	violet red
70°	blue	brown orange
80°	indigo blue	orange yellow
90°	violet	yellow with some orange
100°	violet	yellow

the water-curve. On heating, the curve for the solution descends more rapidly than that for the salt; they intersect each other, and this causes again the pronounced colour effects to appear. As appears from the following table the colours are almost the same as those of the rubidium salt at about 30° to 40° lower temperature.

Temperature	Colours of the transmitted light	Colours of the dispersed light
40°	orange yellow	blue
50°	almost yellow	blue
60°	yellow	blue
70°	green yellow	blue violet
80°	yellow green	violet
90°	green	red violet
100°	blue	yellow brown

While the Cs-, Rb-, and K-salts of the boron fluor hydrogenic acid are sparingly soluble, the Na- and Li-salts dissolve readily in water <sup>1)</sup>.

<sup>1)</sup> Cf. for the further properties: J. H. DE BOER and J. A. M. V. LIEMPT. *Rec. d. tr. chim. des Pays-Bas*, **46**, 124 (1927).

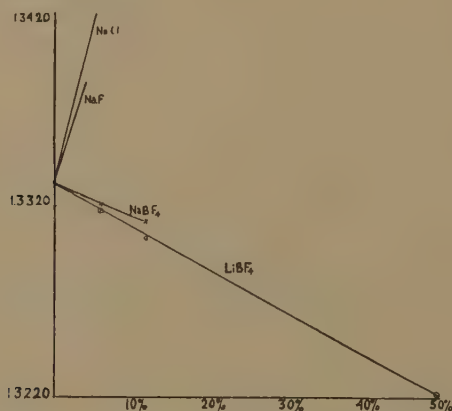


It was more or less to be expected that the indices of refraction of these salts should be still lower, and it might also be expected that the solutions of these salts had a lower index of refraction than that of water.

This appeared actually to be the case; thus the following values were found for the *D*-line at 20° C.:

		Water:	1.3332
NaBF <sub>4</sub>	6 <sup>0</sup> / <sub>0</sub>	solution:	1.3321
	12 <sup>0</sup> / <sub>0</sub>	"	: 1.3312
LiBF <sub>4</sub>	6 <sup>0</sup> / <sub>0</sub>	"	: 1.3318
	12 <sup>0</sup> / <sub>0</sub>	"	: 1.3303
	50 <sup>0</sup> / <sub>0</sub>	"	: 1.3221.

This last value is not so very certain, as the measurement had to be done very rapidly; there were indications that the glass was attacked. As is, however, clear from the adjoined figure, the points lie sufficiently accurately on a straight line.



By way of comparison also the increases of the index of refraction of water on dissolving NaCl or NaF have been drawn.

Also the boron fluor hydrogenic acid itself lowers the index of refraction of water. A solution containing about 20% of this acid gave a value of 1.3284.

Eindhoven, February 1927.

Natuurkundig Laboratorium  
der N.V. Philips' Gloeilampenfabrieken.

**Physics.** — *The Structure of the Calcium Fluoride Band  $\lambda$  6087.* By  
S. GOUDSMIT. (Communicated by Prof. P. ZEEMAN).

(Communicated at the meeting of February 26, 1927).

The most accurate investigation of the structure of the calcium fluoride bands is that by DANJON<sup>1)</sup>, who observed that these bands seem to show an entirely different structure from that of most of the other bands hitherto known. He could examine band  $\lambda$  6087 most accurately, because this band is more easily resolvable than the other bands from this spectrum and is more simply constructed.

On cursory examination this band has the appearance of an ordinary group of bands, the band edges of which form a regular series. DANJON was, however, of the opinion that this could not be the case. For it appears that the bands do not overlap, as in an ordinary group of bands, but that every band seems to stop at the very place where the following band begins. Further DANJON particularly pointed out that the frequencies of the lines of the whole band can be represented by a single formula, with one parameter. According to DANJON we have to do here with one band which presents remarkable intensity anomalies. From the first band edge the intensity decreases regularly, till suddenly an intense line makes its appearance, after which the intensity again slowly diminishes. This is repeated a few times, the mutual distance of the lines at the same time becoming greater.

The purpose of our investigation was to examine whether DANJON's view still appeared to be correct, if measurements were made with greater dispersion than was used by him.

The spectrum was photographed in the second and the third order of a concave grating with a radius of curvature of 6 meters and with 14438 rulings to the inch. The arrangement was that of EAGLE. In the region examined the dispersion in the second order amounted to about 12 Å per cm. and in the third order to about 8 Å per cm.

The greatest difficulty was to find a suitable source of light, and this has not been entirely overcome. The most satisfactory arrangement was an arc, the two carbons of which had a vertical position, the lower (positive) carbon having a perforation filled with calcium fluoride. Use was successfully made of a magnet in the well-known way to "blow" the arc in a definite direction, and to promote in this way the regular

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<sup>1)</sup> A. DANJON, Diplôme d'Etudes sup. Paris (1914).

consumption of the calcium fluoride filling. The arc was operated with a direct current arc, which had to be continually regulated by the hand. Other sources gave the band to be investigated, which is one of the faintest of the spectrum, with too small intensity. The source used had, however, the very great drawback that the lines were fairly diffuse: it is to be regretted that our attempts to overcome this difficulty have not succeeded. The consequence of this was that the resolving power of the grating could not be entirely used; the limit for the resolution was defined by the diffuseness of the lines. In consequence of this the measurements in the third order have no advantages at all over those in the second, on the contrary, they required a longer time of exposure without giving better resolution.

With the times of exposure at which the band under investigation gave the best blackening, varying from 30 to 80 minutes, the neighbouring group of bands  $\lambda$  6064 was already greatly over-exposed, and clearly showed reversals on most photographs.

Fig. 1 shows the intensities of the band as given by DANJON. This sketch is in conformity with his conception that the whole is one band with regular intensity anomalies. This conception finds expression in the figure: leaving the anomalies out of consideration, the intensity decreases regularly towards the tail of the band. This decrease is, however, not real; the appearance is caused by the fact that the lines towards the tail of the band lie further apart with diminishing wavelength, and that owing to this the blackening on the plate seems less. The real course of the intensity is represented by fig. 2. This is an intensity curve of one of the photographs in the second order of the grating made with a Moll-photometer <sup>1)</sup>. Roughly a curve would be obtained about as in fig. 3. The most striking feature is that in the first apparent band the intensity seems to decrease most rapidly, in the following bands this diminution proceeds more and more slowly and at the end all the lines have even about equal intensity so that it is not possible to define there the apparent edges with certainty, as in the beginning. When observing this it should, however, be taken into consideration that in the successive bands the lines lie farther and farther apart, and in consequence of this a seemingly slower decrease of the intensity is caused. As a matter of fact the number of lines in the bands should be taken into account in this comparison.

In view of what precedes it is improbable that DANJON's view should be correct. Nor does it seem that we have to do here with a number of bands each of which stops exactly where the next begins. Probably

<sup>1)</sup> The description of the arrangement for the application of the scale on the photogram, which was also used very successfully in this investigation, is found in KOK and ZEEMAN, These Proc. 27, 884, 1924.



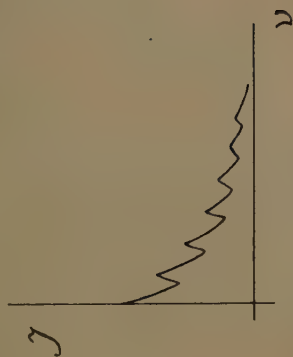


Fig. 1.

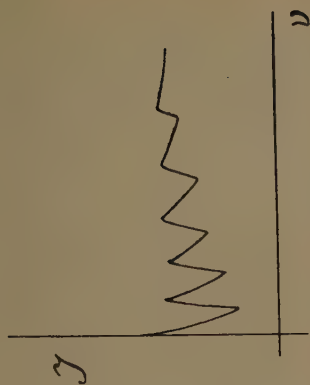


Fig. 3.

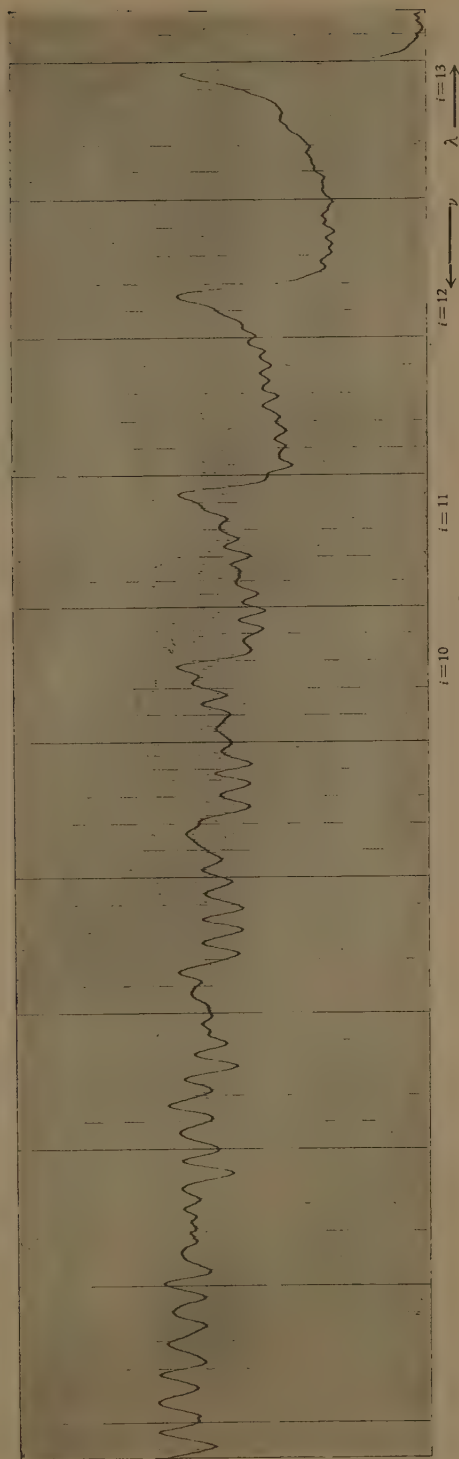


Fig. 2. 1 dividing line = 0.0244 Å

we have to do here with a group of bands of which the successive bands are superposed, but that in this case the lines from the different bands happen to coincide and consequently present the appearance of one continuous band. When this is assumed, it may be understood why the intensity in the successive bands diminishes more and more slowly. This is due to the superposition of lines from the different bands; in the first band the normal intensities are found, in the second the last lines of the first band coincide with those really belonging to the second band, changing their apparent intensities, in the third band lines from the second band produce the same effect, those of the first probably having no longer any influence, and so on. This superposition has not yet much influence for the second band, because the lines in question from the first band have a high number, greater than 33; in the third band, however, it is already very pronounced, because the overlapping extreme lines of the second band start already with the number 13 and are hence rather intense.

There is another reason indicating that probably we are not dealing here with one band. A close examination of the photographs and of the photometer curve reveals certain irregularities, which always become more and more pronounced towards the end of the band. It appears as if the coincidence of lines from the different bands does not take place so accurately as might be supposed at first sight. At different places the lines are diffuse, which seems to suggest "interference" of the lines from the different bands. Near the end of the group of bands this has such a great disturbing effect that it is no longer possible there to identify the lines with certainty.

Even if the conception of the structure of these bands given here, in contrast with that of DANJON, is correct, these bands do not present a normal structure, as will appear in the discussion of the band-formula to be given later. Inasmuch as this is the only known example of bands from this kind of a tri-atomic molecule, it is not yet possible to decide with certainty which interpretation is the correct one.

Before discussing the numerical data, we wish to point out that in consequence of the diffuseness of the lines their measurement could be made much better with the photometer than with the comparator. The edges, however, presented a difficulty. In consequence of there being a region of slight blackening on one side and a region of intense blackening on the other side, the maximum of the curve of intensity for the edges was always slightly displaced towards the latter region, especially at the beginning. The accuracy that could be reached, was no greater than about 0.015 Å.

According to DANJON all the lines of the group of bands can be represented by one formula, an ordinary zero-branch formula:

$$\nu = 16428,24 + 0,004497 n^2 + 0,0000010 n^3 : \dots \quad (1)$$

In accordance with what precedes, our opinion is, however, that this fact is more or less accidental, and that in reality we have to do here with a number of different bands. Each band must then have a formula of its own. From the preceding formula we expect for these bands:

$$\nu = 16428,24 + 0,004497 (m + p)^2 \quad . \quad . \quad . \quad . \quad (2)$$

In this  $p$  is evidently the number that the first line from each band has in DANJON's formula. Hence  $p$  is equal to zero for the first band, and the ordinary zero-branch formula is obtained. The other bands seem to be zero-branch formulae of which the first  $p-1$  lines are absent. They may, of course, also be taken as positive branches, but then an explanation is required why the negative branches are not present. The values of  $p$  are: 0, 34, 47, 56, 63, 69, 74.

Formula (2), however, still rests on the supposition that the lines from the different bands accurately coincide. It would not be easy to interpret the strange series of  $p$ -values. It seems more probable to us that for the derivation of the band formula another fact observed by FABRY <sup>1)</sup> should be utilized. The band edges, the first lines of every band, themselves satisfy again a quadratic formula, namely: <sup>2)</sup>

$$\nu_i = 16428,24 + 0,208,58 (13^2 - i^2) \quad . \quad . \quad . \quad . \quad (3)$$

Remarkable is here the appearance of the integer 13 in this formula. It might be held to be accidental, if the values 13.5, 14 and 14.5 did not occur in other groups of bands in this spectrum. If it is now assumed that formula (1) is valid approximately, and if this is combined with formula (3), we find for the bands:

$$\nu = 16428,24 + 0,004497 (m + 6,807 \sqrt{13^2 - i^2})^2 + \left. \begin{aligned} &+ 0,0000010 (m + 6,807 \sqrt{13^2 - i^2})^3 \end{aligned} \right\} \quad (4)$$

The coinciding of the different bands arises through the fact that the values  $p$  obtained as solutions of the equations

$$0,004497 p^2 + 0,0000010 p^3 = 0,20858 (13^2 - i^2),$$

come pretty near to whole numbers, especially in the beginning. As the deviation from a whole number must be pretty great to have a disturbing influence, this may very well be only accidental.

It should still be pointed out that the structure of the bands renders it probable that the values of  $m$  must be integers, also the numbering of the values  $i$  is integral in this band.

The table gives the wave-lengths in the first part of the band from new measurements in the region where the measurement is still pretty

<sup>1)</sup> Journ. de Phys. 4, 245, 1905.

<sup>2)</sup> In this formula  $i$  passes through the values 13, 12 etc. to 0. If it is desired to have the numbering in inverse order,  $(13-i)$  should be substituted for  $i$ .



<i>n</i>	<i>m</i>		<i>n</i>	<i>m</i>	
0	<i>i</i> = 13   0	$\lambda$ 6087.08 Å	43	<i>i</i> = 12   9	$\lambda$ 6083.98 Å
—	—		44	10	.83
—	—		45	11	.67
29	29	5.71	46	12	.52
30	30	.62	47	<i>i</i> = 11   0	.37
31	31	.51	48	1	.21
32	32	.39	49	2	.05
33	33	.27	50	3	2.86
34	<i>i</i> = 12   0	.16	51	4	.70
35	1	—	52	5	.52
36	2	—	53	6	.34
37	3	4.80	54	7	.16
38	4	.66	55	8	1.98
39	5	.55	56	<i>i</i> = 10   0	.78
40	6	.41	57	1	.60
41	7	.27	58	2	.41
42	8	.12	59	3	.20

certain. The lines between  $n=0$  and  $n=29$  could not be resolved. In DANJON the resolution into lines did not begin before  $n=47$ .

Let us finally consider the other bands investigated by DANJON. According to a communication by DANJON he has succeeded in resolving another group of bands, viz.  $\lambda$  6051, also into lines. For the lines he gives the probable formula:

$$\nu = 16526,1 + 0,006233 n^2 + 0,0000083 n^3.$$

For the edges the formula is:

$$\nu_i = 16526,1 + 0,2030 (14^2 - i^2).$$

According to our conception the following formula would be written for this group of bands:

$$\nu = 16526,1 + 0,006233 (m + 5,707 \sqrt{14^2 - i^2})^3 + 0,0000083 (m + 5,707 \sqrt{14^2 - i^2})^3.$$

For the other groups of bands only the edges have been measured. The formulae for these are:

$$\lambda \text{ 6064,61 : } \nu_i = 16489,1 + 0,1895 (15,5^2 - i^2)$$

$$\lambda \text{ 6037,17 : } \nu_i = 16564,1 + 0,2279 (13,5^2 - i^2).$$

If the formula (4) given here renders the correct conception of the bands, it would be probable that we have to do here with two moments of momentum, one with a quantum number  $m$  and one with the quantum number 13, of which the projection normal to  $m$  is equal to  $i$ , the projection along  $m$  is then  $\sqrt{13^2 - i^2}$ . Neither the theory nor the experiments are, however, sufficient to give, with certainty, a theoretical interpretation. Probably an electron moment of momentum also plays a part here, for, as is known, these bands, in contrast with most others, show a large ZEEMAN-effect.

I am greatly indebted to Prof. R. FORTRAT (Grenoble) for suggesting this investigation to me, and to Prof. P. ZEEMAN for his encouragement, advice, and for the necessary instruments which he placed at my disposal.

*Amsterdam, Laboratory "Physica".*

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**Physics.** — *The vapour pressures of solid and liquid neon.* By C. A. CROMMELIN and R. O. GIBSON. Communication N<sup>o</sup>. 185*b* from the Physical Laboratory at Leiden. (Communicated by Prof. W. H. KEESOM).

(Communicated at the meeting of February 26, 1927).

§ 1. *Introduction.* During the purification of some neon by a method similar to that already described by one of us (C. A. C.)<sup>1)</sup> it was observed that the vapour pressure of the solid neon at the temperature of boiling hydrogen ( $\pm 20^{\circ}$  K.) was about 4 cm, whilst TRAVERS and JAQUEROD give  $\pm 1.2$  cm. As a matter of fact TRAVERS and JAQUEROD<sup>2)</sup> give the following values

20 <sup>o</sup> .4 K.	12.8 mm Hg and
15 <sup>o</sup> .65 K.	2.4 mm Hg.

The latter were the results of preliminary measurements only and, as no others have been made, it seemed desirable to make an extended series of determinations of the vapour pressures of solid neon.

The vapour pressures of the liquid between the triple and critical points have been measured formerly in the Physical Laboratory at Leyden<sup>3)</sup>.

§ 2. *Details of the measurements.* The apparatus used was similar to that already described by CATH<sup>4)</sup>.

Two sets of apparatus were used, one filled with neon taken from a cylinder of the gas purified by the method mentioned above, and the other with neon that had been further fractionated by condensing some neon from the cylinder and allowing a middle fraction to evaporate directly into the previously washed and evacuated apparatus. The two sets were placed side by side in the cryostat and measured alternately. Only slight unsystematic differences, well within the experimental error, were found in the vapour pressures of the two samples of neon, indicating that they were of the same purity.

The measurements up to 20<sup>o</sup>.4 K. were made in a liquid hydrogen cryostat, the temperatures being measured by means of one or two

<sup>1)</sup> C. A. CROMMELIN, Rec. des Trav. chim. des Pays-Bas (4) **42**, 814, 1923; Comm. Leiden N<sup>o</sup>. 162c.

<sup>2)</sup> M. W. TRAVERS and A. JAQUEROD, Phil. Trans. A **200**, 175, 1903.

<sup>3)</sup> H. KAMERLINGH ONNES and C. A. CROMMELIN, These Proceedings **18**, 515; Comm. Leiden N<sup>o</sup>. 147*d*; P. G. CATH and H. KAMERLINGH ONNES, These Proceedings **20**, 1160; Comm. Leiden N<sup>o</sup>. 152*b*.

<sup>4)</sup> P. G. CATH, These Proceedings **21**, 656; Comm. Leiden N<sup>o</sup>. 152*d*.



platinum resistance thermometers. The pressures were measured by reading the heights of the mercury in the two arms of the manometer with a carefully levelled cathetometer and standard scale.

A hydrogen vapour cryostat was used for the measurements above the boiling point of hydrogen.<sup>1)</sup>

§ 3. *Purity of the neon.* On several occasions vapour pressure measurements at the same temperature but with different volumes of the phases were made. The slight, if any, differences found were quite irregular and well inside the experimental error.

§ 4. *Experimental accuracy.* The accuracy of the temperature measurement was somewhat higher in the liquid cryostat than in the vapour cryostat (0.01 and 0.02 to 0.03 degree respectively), which appeared from the constancy of the temperatures and the concordance of the resistance thermometers. In the region of the higher temperatures the vapour pressures could only be determined to 1 mm, which becomes clear when one takes into consideration that e.g. at  $-248^{\circ}\text{C.}$ , 0.01 degree difference in temperature means 1.5 mm difference in pressure.

§ 5. *Results.* The results of the measurements in the solid and liquid regions, together with those previously published, are given in table I.

The temperatures are given in degrees KELVIN, while  $-273^{\circ}.09\text{C.}$  is assumed for the absolute zero. The pressures are given in international cm mercury and in international atmospheres. At Leyden the international atmosphere is equivalent with 75.9529 local cm mercury.

§ 6. *Triple point.* From a large scale graph of the present results the following values of the triple point constants were found:

$$\theta = -248^{\circ}.52\text{C.}, \quad T = 24^{\circ}.57\text{K.}, \quad p = 32.35\text{ int. cm.}$$

During one days measurements when special attention was fixed on the region round the triple point, it was observed that at one temperature the neon in one apparatus, that into which the neon had been distilled, was solid whilst that in the other, containing neon from the cylinder, was still liquid. Both were obtained solid on lowering the temperature still further, and on warming both appeared to melt at the same time. The phenomena was therefore due to supercooling and not, as was first thought, to impurities in the neon from the cylinder.

We are grateful to several assistants of the laboratory for their ready assistance in the measurement of temperatures, and one of us (R. O. G.) wishes to acknowledge his indebtedness to the SALTERS' Company of London for a Fellowship which made participation in this work possible.

<sup>1)</sup> H. KAMERLINGH ONNES, These Proceedings 19, 1049; Comm. Leiden N<sup>o</sup>. 151a; H. KAMERLINGH ONNES and C. A. CROMMELIN, These Proceedings 23, 1185; Comm. Leiden N<sup>o</sup>. 154c.

TABLE I.

	$\Theta$	$T$	Pressure		
			int. cms Hg	int. atm.	
Solid	—257.62° C.	15.47° K.	0.055	0.00072	
	—256.79	16.30	0.13	0.0017	
	—256.46	16.63	0.21	0.0028	
	—255.79	17.30	0.37	0.0049	
	—255.43	17.66	0.51	0.0067	
	—254.92	18.17	0.78	0.0103	
	—254.63	18.46	0.98	0.0129	
	—254.07	19.02	1.49	0.0196	
	—253.64	19.45	2.00	0.0263	
	—253.30	19.79	2.53	0.0333	
	—253.22	19.87	2.71	0.0357	
	—253.16	19.93	2.82	0.0371	
	—252.62	20.47	4.00	0.0527	
	—251.24	21.85	9.1	0.120	
	—250.84	22.25	11.1	0.146	
	—250.22	22.87	14.8	0.195	
	—249.62	23.47	19.5	0.257	
	—249.09	24.00	25.0	0.329	
	—248.84	24.25	27.9	0.367	
	—248.58	24.51	31.5	0.415	
	—248.56	24.53	31.7	0.417	
Liquid	Comm. 147d	—248.51	24.58	32.4	0.427
		—248.51	24.58	32.50	0.4276
		—248.29	24.80	35.0	0.461
		—248.10	24.99	37.3	0.491
		—247.82	25.27	41.0	0.540
	" 147d	—247.49	25.60	45.16	0.5942
		—247.33	25.76	48.6	0.640
	" 147d	—246.66	26.43	60.52	0.7963
	" 147d	—245.88	27.21	76.71	1.0094
		—245.79	27.30	79.1	1.041
	" 147d	—245.68	27.41	81.62	1.0740
	" 152b	—243.69	29.40		1.888
	" "	—241.77	31.32		2.980
	" "	—240.25	32.84		4.173
	" "	—236.82	36.27		7.970
	" "	—233.60	39.49		13.213
	" "	—231.71	41.38		17.428
	" "	—229.26	43.83		24.305
	" "	—228.66	44.43		26.049

Measurements of H. KAMERLINGH ONNES and C. A. CROMMELIN, These Proceedings 18, 515; Comm. Leiden N<sup>o</sup>. 147d.

Measurements of P. G. CATH and H. KAMERLINGH ONNES, These Proceedings 20, 1160; Comm. Leiden N<sup>o</sup>. 152b.

**Mineralogy.** — *A contribution regarding the Mineralogical Composition of some of the Soils of the Netherlands.* By J. H. DRUIF.  
(Communicated by Prof. L. RUTTEN.)

(Communicated at the meeting of February 26, 1927).

I have for a considerable time been engaged on an inquiry into the mineralogical composition of a number of Netherlands soils and that of some of Belgium, with a view to collect data, that might aid an interpretation of the formation of the so-called Limburg Loess. It seemed to me useful to publish some results of my inquiry, although it is not quite ended yet.

My research concerned 46 samples, to wit: 14 Boulder clay from different provinces, 15 Limburg-Loess, 5 pre-glacial clays also from different provinces, 7 weathering soils from S. Limburg, and 5 Senonian rocks from S. Limburg, of which 2 Maastrichtien and 3 Gulpenien, (resp. Mb, Mc and Cr, étages).

The Belgian soils may be just as well left out of consideration.

The accompanying table gives a list of the minerals found, also the groups of soils in which they occurred, and a rough determination of their relative quantities. Besides this I specify the following results, as being the most important outcome of this part of my inquiry.

a. SCHROEDER VAN DER KOLK's quantitative relations<sup>1)</sup> between the heavy minerals in soils containing northern material and in soils exclusively built up of southern material, have been found by the present writer to be generally correct.

b. RETGERS's view,<sup>2)</sup> originally also adopted, but ultimately relinquished, by SCHROEDER VAN DER KOLK<sup>3)</sup> has after all been corroborated, for, as RETGERS suspected, typical northern minerals have been detected in our soils, while at least three specifically southern ones were met with. One mineral appeared to occur preferably and in larger quantities in southern soils.

c. There is, in my judgment, unmistakably a resemblance in the mineralogical composition of Boulderclay and the so-called Limburg Loess.

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<sup>1)</sup> J. L. C. SCHROEDER VAN DER KOLK, Bijdrage tot de karteering onzer zandgronden 1, K. A. v. W. Verh. Tweede Sectie Dl. 4, N<sup>o</sup>. 4. 1895.

<sup>2)</sup> J. W. RETGERS, De samenstelling van het Duinzand, K. A. v. W., Verh. Dl. 29 '91.

<sup>3)</sup> J. L. C. SCHROEDER VAN DER KOLK, Bijdrage tot de karteering onzer zandgronden 3, K. A. v. W., Verh. Tweede Sectie Dl. 6, N<sup>o</sup>. 4. '98.

Table of the Minerals found.

Name	Boulder-clay	Pre-glacial	So-called Loess	Chalk	Weathering soil
Aegirin	+	—	—	—	—
Anatase	l +	+	l +	—	+
Andalusite	+	—	+	—	+
Apatite	+	—	—	—	—
Arfvedsonite	+	—	l +	—	—
Barkevikite (?) <sup>2)</sup>	l +	—	v l +	—	—
Biotite	+	+	+	—	—
Calcite	+	—	—	—	—
Cyanite <sup>1)</sup>	+	—	+	—	?
Disthene	m +	l +	m +	v l +	+
Dumortierite	—	—	—	v l +	v l +
Epidote	m +	l +	m +	—	l +
Glauconite	+	+	+	l +	l +
Glaucophanes	+	—	+	—	—
Granate	m +	+	+	v l +	v l—l +
Hornblende (gr.)	v m +	+	v m +	v l +	v l +
Hornblende (br.)	+	—	+	—	—
" (no colour)	+	?	+	—	+
Hypersthene	+	—	—	—	—
Ilmenite	+	+	+	+	+
Korund	—	—	—	—	+
Quartz	v m +	v m +	v m +	+	m +
Lazulith	—	—	—	—	l +
Magnetite	+	+	+	+	+
Microklin	+	+	+	+	+
Muscovite	+	+	+	l +	l +
Ottrelite	—	—	—	—	+ <sup>3)</sup>
Orthoclase	+	+	+	+	+
Piemontite	l +	—	l +	—	—
Plagioclase	+	+	+	+	+
Pyrite	+	+	—	+	—
Pyroxene	+	+	l +	—	—
Rutile	m +	+	m +	+	v m +
Sillimannite	+	—	+	—	—
Spinel	l +	—	l +	—	—
Staurolite	m +	+	m +	l +	m +
Thulite	+	—	l +	—	—
Titan-Augite	+	—	l +	—	—
Titanite	+	—	+	—	+
Vesuvian (?)	—	—	v l +	—	—
Zircon	v m +	m +	v m +	+	v m +
Zoisite	+	—	+	—	—

m = much; v m = very much; l = little; v l = very little; + = present; — = absent;  
? = not quite certain.

<sup>1)</sup> Cyanite only for the distinctly blue variety.

<sup>2)</sup> It is not precluded that the mineral in question is a basaltic Hornblende.

<sup>3)</sup> In strictness, no weathering soil, but a river-deposit near Caberg.



The results of this inquiry appear to us to establish that the following minerals are specifically northern: Manganese-Epidote, which appears in two varieties, viz. Piemontite and Thulite; the Amphibole-variety Arfvedsonite (and incidentally Barkevikite); the Glauco-phane, especially when there are many specimens in the sample, and the Titanous-Augite.

VAN BAREN<sup>1</sup>) records that he rarely recognized Glauco-phane in the Senonian; however, I have not succeeded in detecting this mineral in any southern soil, (not in the Belgian soil either!) but at any rate it occurs in the northern soils and in rather large quantity even in Loess.

Only in southern soils did I find Lazulith (Klaprotite) (weathering soils), Dumortierite, and Ottrélite, while the mineral Anatase evinced a distinct preference for southern soils, again especially as to the number of specimens per sample.

*From the Geol. Institute of the State-University at Utrecht.  
Utrecht, February 1927.*

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<sup>1</sup> J. VAN BAREN, *De bodem van Nederland*, Deel II, Kwartair, 19—22 stuk. 1926.

**Mathematics.** — *Fusion of the existing Theories of the Irrational Number into a New Theory.* By Prof. FRED. SCHUH. (Communicated by Prof. D. J. KORTEWEG).

(Communicated at the meeting of February 26, 1927).

**1. Introduction.** In the existing theories of the irrational number as those of CANTOR, DEDEKIND, BAUDET and WEIERSTRASS (cf. my book: "Het Getalbegrip, in het bijzonder het Onmeetbare getal, met toepassingen op de Algebra, de Differentiaal- en de Integraalrekening") definitions are given of irrational numbers, of the operations addition and multiplication of real (rational or irrational) numbers and of the relation greater. It follows from these definitions that *for the real numbers the same calculation-rules (and the same properties connected with the relation greater) are valid as for the rational numbers* and that for the system of the real numbers the following *theorem of the upper boundary holds good*:

*If  $S$  is a non-empty set of real numbers all of which are less than or equal to the same real number (bounded on the right), there exists a real number  $U$  (upper boundary of  $S$ ), with the following two properties:*

- 1. No number of  $S$  is  $> U$ ;*
- 2. If  $U'$  is a real number  $< U$ ,  $S$  contains at least one number which is  $> U'$ .*

It is at once clear that *there can only be one number which corresponds to the definition of upper boundary.*

As I have explained in my "Getalbegrip", for the application of the irrational numbers we have only to do with these results and not with the meaning of addition, etc. For this reason the theorem of the upper boundary is the keystone of each of the above mentioned theories of the irrational number and plays a fundamental part in the Algebra, the Differential and the Integral calculus. Instead of it we might also take a theorem that is equivalent to the theorem of the upper boundary, as the theorem of BOLZANO or the general principle of convergence of CAUCHY. However, the theorem of the upper boundary (or that of the lower boundary, which comes about to the same) seems to me to be the most suitable.

It would be very unpracticable to introduce the irrational number into Algebra and Analysis in another way than via the theorem of the upper boundary (or an equivalent theorem), e. g. by defining  $a^x$  for an irrational value of  $x$  as a convergent sequence of CANTOR or a section of DEDEKIND, or by proving the theorem about the zero-point of a

continuous function which can assume positive and negative values, by producing that zero-point of the function as a convergent sequence of CANTOR or a section of DEDEKIND. This would give the wrong impression that there exists an Algebra according to CANTOR and one according to DEDEKIND. As all the theories of the irrational number come together in the theorem of the upper boundary, in Algebra we have nothing to do with the chosen theory.

The purpose of this paper is to show *that we can make the different theories of the irrational number concur still more*, so that the part played by the theorem of the upper boundary becomes still greater. By so doing the theories of the irrational number approach each other more *because the definitions of addition and multiplication become the same*. The difference between the various theories of the irrational number only remains in the definition of this numbers, in the definition of "greater" and in a few proofs. In this way the theory of the irrational number (if we stop where it coincides with other theories) becomes considerably shorter and simpler, because addition and multiplication no longer belong to it but must be reckoned among the applications<sup>1)</sup>.

**2. Contents of a theory of the irrational number.** We assume that the *rational numbers* have been introduced and that for them the well known fundamental properties (cf. my "Getalbegrip", § 18) have been proved.

A theory of the irrational number means (according to the ideas developed in this paper) an extension of the system of the rational numbers to that of the *real numbers* and such a definition of "greater" in the new system that the following properties are valid:

a. For any two real numbers  $\alpha$  and  $\beta$  one and only one of the following three relations holds good:

$\alpha = \beta$  (both numbers are the same, also written as  $\beta = \alpha$ ),

$\alpha > \beta$  (also written as  $\beta < \alpha$ ),

$\beta > \alpha$  (also written as  $\alpha < \beta$ ).

b. If  $\alpha > \beta$  and  $\beta > \gamma$ , we have  $\alpha > \gamma$  (transitive property).

c. If  $\alpha$  is a real number there always exists a rational number  $> \alpha$ .

d. If  $\alpha$  is a real number, there always exists a rational number  $< \alpha$ .

e. If  $\alpha$  and  $\beta$  are real numbers and if  $\alpha < \beta$ , there always exists a rational number  $c$ , so that  $\alpha < c < \beta$ .

f. For the system of the real numbers the theorem of the upper boundary holds good.

The property a. includes that the definition of "greater" given for the real numbers, if applied to two rational numbers, leads to the same result as the definition of "greater" for rational numbers.

<sup>1)</sup> A more elaborate treatment and a discussion of the connection with the existing theories can be found in the periodical "Christiaan Huygens".

If in a definite theory (e.g. that of CANTOR) the five above mentioned properties have been proved <sup>1)</sup>, this theory may be considered as finished because its continuation is the same as for another theory.

### 3. Enclosure of a real number between two rational numbers.

Relating to this we shall prove the following property (always starting from the properties of  $N^0.2$ ):

*If  $a$  is a given real number and  $v$  a given positive rational number, we can always determine a rational number  $a$  so that  $a < a < a + v$ .*

As the validity of this property is at once apparent if  $a$  is rational, we shall suppose  $a$  to be irrational. According to the properties c. and d. of  $N^0.2$  there are rational numbers  $b$  and  $c$  so that  $b < a < c$ . The numbers  $b + nv$ , in which we can choose for  $n$  any positive integer or 0, contain only a finite number  $< c$ , hence also a finite number  $< a$  (according to the property b. of  $N^0.2$ ). Hence among the numbers  $b + nv$  that are  $< a$  there is one greatest. If this is  $a$  we have  $a < a < a + v$ , as  $a = a + v$  is impossible,  $a$  being irrational.

*4. If  $a$  is a given positive real number and  $v$  is a given rational number  $> 1$ , we can always determine a positive rational number  $a$  so that  $a < a < av$ .*

According to the property e. of  $N^0.2$  there exists a rational number  $b$ , so that  $0 < b < a$ . According to  $N^0.3$  there exists a rational number  $a$ , so that  $a < a < a + b(v-1)$ . Hence  $b < a < bv$ , if  $a < b$ , and  $a < a < av$ , if  $b \equiv a$ .

**5. Definition of the addition of real numbers.** Let  $\alpha$  and  $\beta$  be two (equal or unequal) real numbers; let  $A$  be the set of the rational numbers  $a < \alpha$  and  $B$  the set of the rational numbers  $b < \beta$ . According to the property d. of  $N^0.2$  neither  $A$  nor  $B$  is empty so that the set  $A + B$  of the numbers  $a + b$  is not empty either. Let  $a'$  be a rational number  $> \alpha$  and  $b'$  a rational number  $> \beta$ . From  $a < \alpha$  and  $\alpha < a'$  it follows in connection with the transitive property b. of  $N^0.2$ , that  $a < a'$ . In the same way  $b < b'$ , hence  $a + b < a' + b'$ , so that the set  $A + B$  is bounded on the right and therefore has an upper boundary. This upper boundary, which we shall call  $\alpha + \beta$ , defines the sum of the two real numbers  $\alpha$  and  $\beta$ .

6. If  $a + b$  is a number of the set  $A + B$  of  $N^0.5$  and  $a_1$  is a rational number so that  $a < a_1 < \alpha$ , also  $a_1 + b$  is a number of  $A + B$ . We have, therefore,  $a_1 + b \equiv \alpha + \beta$  (as  $\alpha + \beta$  is the upper boundary of  $A + B$ ), hence  $a + b < \alpha + \beta$  (according to  $a + b < a_1 + b$  and the transitivity).

Let inversely  $c$  be a rational number  $< \alpha + \beta$ . If  $d$  is a rational

<sup>1)</sup> The proofs of these properties are not given in this paper as they are also given in existing theories. They may be found in a paper destined for "Christiaan Huygens".



number so that  $c < d < a + \beta$ , according to the property of  $N^0$ . 3 we can define the rational numbers  $a$  and  $b$  such that

$$a < a < a + \frac{1}{2}(d - c), \quad b < \beta < b + \frac{1}{2}(d - c).$$

If we represent the third members of these inequalities resp. by  $a'$  and  $b'$ , we have  $a' + b' = a + b + d - c$ . From  $a' > a$ ,  $b' > \beta$  it follows that  $a'$  is greater than any number of  $A$  and  $b'$  greater than any number of  $B$ , hence  $a' + b'$  greater than any number of  $A + B$ . Consequently  $a' + b' \equiv a + \beta$  (according to the definition of the upper boundary). As  $d < a + \beta$ , we have, therefore,  $a' + b' > d$ , hence  $a + b > c$ . Consequently  $c - a < b$ , hence  $c - a < \beta$  (as  $b < \beta$ ), so that  $c - a$  is a number of  $B$ . As  $c = a + (c - a)$ ,  $c$  is a number of  $A + B$ . We find accordingly:

*The set  $A + B$  of  $N^0$ . 5 (formed by the numbers  $a + b$ , where  $a$  is an arbitrary rational number  $< a$  and  $b$  an arbitrary rational number  $< \beta$ ) is the same as that of the rational numbers  $< a + \beta$ .*

As an immediate consequence  $a' + b' \equiv a + \beta$  if  $a'$  is a rational number  $\equiv a$  and  $b'$  a rational number  $\equiv \beta$ . For  $a' + b'$  is greater than any number of  $A + B$ ; hence it is not a number of  $A + B$  and does not satisfy the relation  $a' + b' < a + \beta$ .

## 7. Fundamental properties of addition. These are:

I. *From any two real numbers  $a$  and  $\beta$  we can derive one and only one real number  $a + \beta$  by addition.*

II.  $a + \beta = \beta + a$  (commutativity of addition).

III.  $(a + \beta) + \gamma = a + (\beta + \gamma)$  (associativity of addition).

IV.  $a + 0 = a$  (modulus-property of addition).

V. *If  $a < \beta$ , then  $a + \gamma < \beta + \gamma$ .*

The validity of I appears from the fact that the definition of addition of real numbers given in  $N^0$ . 5, applied to two rational numbers, leads to the same result as the earlier addition of rational numbers.

The validity of II is at once evident from the corresponding property of the rational numbers.

The same holds good for III. For if we represent a rational number  $< a$ ,  $< \beta$  or  $< \gamma$  resp. by  $a$ ,  $b$ ,  $c$ , according to the property of  $N^0$ . 6 a rational number  $< a + \beta$  is the same as a number of the form  $a + b$ . Consequently  $(a + \beta) + \gamma$  is the upper boundary of the set of the numbers  $(a + b) + c$ . In the same way  $a + (\beta + \gamma)$  is the upper boundary of the set of the numbers  $a + (b + c)$ . Both sets are the same and have, therefore, the same upper boundary.

If  $a$  is a real number and if  $a$  and  $b$  are rational numbers so that  $a < a$ ,  $b < 0$ , we have  $a + b < a$ , hence  $a + b < a$ . If, inversely,  $c$  is a rational number  $< a$  and  $a$  a rational number so that  $c < a < a$ , we have  $c = a + (c - a)$  where  $a < a$  and  $c - a < 0$ . The set of the numbers  $a + b$  ( $a$  rational and  $< a$ ,  $b$  rational and  $< 0$ ), that has  $a + 0$  as upper boundary, is, therefore, the same as the set of the rational numbers  $< a$ . Hence  $a + 0 = a$ . In this way IV is proved.

If  $\alpha < \beta$ , we can determine the rational numbers  $p$  and  $q$  so that  $\alpha < p < q < \beta$ . If  $\gamma$  is a given real number, according to the property of  $N^0$ . 3 we can determine the rational number  $c$  so that  $c < \gamma < c + q - p$ . According to the property of  $N^0$ . 6  $\beta + \gamma > q + c$ , and from the remark at the end of  $N^0$ . 6 it follows that  $\alpha + \gamma \leq p + (c + q - p) = q + c$ , whence  $\alpha + \gamma < \beta + \gamma$ . In this way V is proved.

**8. Subtraction of real numbers.** The possibility and unambiguity of subtraction rests on the fundamental properties I—IV of  $N^0$ . 7 and

VI. If  $\alpha$  is a given real number, there exists at least one real number  $\xi$  which satisfies  $\alpha + \xi = 0$  (possibility of subtraction from 0).

If we represent a rational number  $> \alpha$  by  $a'$ , the set  $S$  of the numbers  $-a'$  is bounded on the right (as all these numbers are  $< -\alpha$ , if  $\alpha$  is a rational number  $< \alpha$ ). Hence the set has an upper boundary. We shall call this  $\xi$ . If  $a'$  and  $p$  are rational numbers so that  $a' > p > \alpha$ , we have  $-p \leq \xi$  (as  $-p$  is a number of  $S$ ); as  $-a' < -p$  we may write  $-a' < \xi$ . If inversely  $b$  is a rational number  $< \xi$ , there exists such a rational number  $a'$  that  $a' > \alpha$  and  $-a' > b$  (according to the definition of upper boundary); consequently  $-b > a'$ , hence  $-b > \alpha$ , so that  $b$  is the opposite of a rational number  $> \alpha$ . The set of the rational numbers  $< \xi$  is, therefore, the same as that of the numbers of the form  $-a'$  where  $a'$  is rational and  $> \alpha$ . From this follows that  $\alpha + \xi$  is the upper boundary of the set of the numbers  $\alpha + (-a') = -(a' - \alpha)$  ( $a'$  rational and  $< \alpha$ ,  $a'$  rational and  $> \alpha$ ). As  $a' - \alpha$  is positive and can assume any positive value (according to the property of  $N^0$ . 3),  $\alpha + \xi$  is the upper boundary of the set of all negative rational numbers, whence  $\alpha + \xi = 0$ . In this way VI is proved.

From VI we can further deduce that  $\beta - \alpha = \beta + (-\alpha)$  where  $-\alpha$  (the opposite of  $\alpha$ ) is an abbreviation for  $0 - \alpha$ .

**9.** From  $\alpha + \xi = 0$  and  $\alpha > 0$  follows  $0 = \alpha + \xi > 0 + \xi = \xi$ , hence  $0 > \xi$ , so that the opposite of a positive real number is negative. In the same way it appears that the opposite of a negative real number is positive.

From

$$\{-\alpha + (-\beta)\} + (\alpha + \beta) = (-\alpha + \alpha) + (-\beta + \beta) = 0 + 0 = 0$$

there follows:

$$-(\alpha + \beta) = -\alpha + (-\beta),$$

so that the opposite of the sum of two real numbers is the sum of the opposites of these numbers.

**10. Definition of the multiplication of real numbers.** Let  $\alpha$  and  $\beta$  be two positive real numbers,  $A$  the set of the positive rational numbers  $a < \alpha$  and  $B$  the set of the positive rational numbers  $b < \beta$ . According to the property e. of  $N^0$ . 2 neither  $A$  nor  $B$  is empty so that the set  $AB$  of the numbers  $ab$  is not empty either. If  $a'$  and  $b'$  are rational numbers that are  $> \alpha$  resp.  $> \beta$ , we have  $a < a'$  and  $b < b'$ , hence

$ab < a'b'$ . Accordingly the set  $AB$  is bounded on the right and hence has an upper boundary. We shall call this  $a\beta$  and define in this way the product of two positive real numbers.

*Supplementary definitions.* If  $\alpha$  is positive and  $\beta$  negative (hence  $-\beta$  positive), we define  $\alpha\beta$  as  $-\{\alpha(-\beta)\}$ . Likewise we define  $\alpha\beta = -\{(-\alpha)\beta\}$ , as  $\alpha$  negative and  $\beta$  positive. If  $\alpha$  and  $\beta$  are both negative we define  $\alpha\beta = (-\alpha)(-\beta)$ .

If  $\alpha = 0$  or  $\beta = 0$ ,  $\alpha\beta$  is defined as 0.

11. In a similar way as in  $N^0$ . 6 it appears that a number  $ab$  of the set  $AB$  of  $N^0$ . 10 is less than  $a\beta$  (where  $\alpha$  and  $\beta$  are positive real numbers). Let  $c$  be a positive rational number  $< a\beta$ . If  $d$  is a rational number so that  $c < d < a\beta$  and  $e$  is a rational number so that  $1 < e < \frac{d}{c}$ , we have  $\frac{d}{c} = ef$  where  $f$  is a rational number  $> 1$ . According to the property of  $N^0$ . 4 we can determine the positive rational numbers  $a$  and  $b$  such that

$$a < \alpha < ae, \quad b < \beta < bf.$$

Consequently  $ae$  is greater than any number of  $A$  and  $bf$  greater than any number of  $B$ , hence  $abef$  is greater than any number of  $AB$  so that  $abef = a\beta$ . As  $d < a\beta$  we have  $abef > d$ , hence  $ab > c$ . Accordingly  $\frac{c}{a} < b$ , hence  $\frac{c}{a} < \beta$ , so that  $\frac{c}{a}$  is a number of  $B$ . Owing to  $c = a \cdot \frac{c}{a}$ ,  $c$  is a number of  $AB$ .

Accordingly :

If  $\alpha$  and  $\beta$  are positive real numbers, the set  $AB$  of the numbers  $ab$  (where  $a$  and  $b$  are arbitrary positive rational numbers resp.  $< \alpha$  and  $< \beta$ ) is the same as that of the positive rational numbers  $< a\beta$ .

**12. Fundamental properties of multiplication.** These are :

VII. From any two real numbers  $\alpha$  and  $\beta$  one and only one real number  $\alpha\beta$  may be derived through multiplication.

VIII.  $\alpha\beta = \beta\alpha$  (commutativity of multiplication).

IX.  $(\alpha\beta)\gamma = \alpha(\beta\gamma)$  (associativity of multiplication).

X.  $\alpha(\beta + \gamma) = \alpha\beta + \alpha\gamma$  (distributive property).

XI.  $\alpha \cdot 1 = \alpha$  (modulus-property of multiplication).

XII. If  $\alpha > 0$  and  $\beta > 0$ , then  $\alpha\beta > 0$ .

*Proof of VII.* The definition of multiplication of positive real numbers given in  $N^0$ . 10, if applied to two positive rational numbers, leads to the same result as the earlier multiplication of positive rational numbers. As also the supplementary definitions of  $N^0$ . 10 are in accordance with the properties of the rational numbers, multiplication is an unambiguous operation.

*Proof of VIII.* This rests on the corresponding property of rational numbers.

*Proof of IX.* If  $a, \beta, \gamma$  are all positive, the proof is quite analogous to that of the fundamental property III (cf. N<sup>o</sup>. 7). If one (or more) of the numbers  $a, \beta, \gamma$  is zero,  $(a\beta)\gamma$  as well as  $a(\beta\gamma)$  is zero. If  $a, \beta, \gamma$  are all  $\neq 0$  but not all positive, the validity of  $(a\beta)\gamma = a(\beta\gamma)$  follows from the validity for positive real numbers and the supplementary definitions of N<sup>o</sup>. 10.

*Proof of X.* We shall first suppose that  $a, \beta$  and  $\gamma$  are all three positive. It appears from N<sup>o</sup>. 6 that  $a(\beta + \gamma)$  is the upper boundary of the set  $S$  of the numbers  $a(b + c)$  where  $a, b$  and  $c$  are arbitrary positive rational numbers resp.  $< a, < \beta$  and  $< \gamma$ . From the property of N<sup>o</sup>. 11 it is further evident that  $a\beta + a\gamma$  is the upper boundary of the set  $T$  of the numbers  $a_1 b + a_2 c$  where  $a_1$  and  $a_2$  are rational numbers between 0 and  $a$ . As  $a(b + c) = ab + ac$ , any number of  $S$  is also a number of  $T$ . If  $a_1 \leq a_2$  we have  $a_1 b + a_2 c \leq a_2(b + c)$ , so that to any number  $t$  of  $T$  there corresponds a number of  $S$  that is  $\geq t$ . Hence  $S$  and  $T$  have the same upper boundary so that  $a(\beta + \gamma) = a\beta + a\gamma$ .

If  $a = 0, \beta = 0$  or  $\gamma = 0$ , both  $a(\beta + \gamma)$  and  $a\beta + a\gamma$  are resp. 0,  $a\gamma$  or  $a\beta$ , so that in this case X holds good. We may therefore suppose  $a, \beta$  and  $\gamma$  all three  $\neq 0$ .

If  $a$  and  $\beta$  are positive,  $\gamma$  negative and  $\beta + \gamma \geq 0$ , then  $-\gamma$  is positive (cf. N<sup>o</sup>. 9). As X holds good for  $a > 0, \beta \geq 0, \gamma > 0$ , we have:

$$\begin{aligned} a(\beta + \gamma) &= \{a(\beta + \gamma) - a\gamma\} + a\gamma = \{a(\beta + \gamma) + a(-\gamma)\} + a\gamma = \\ &= a\{\beta + \gamma + (-\gamma)\} + a\gamma = a\beta + a\gamma. \end{aligned}$$

In connection with II (cf. N<sup>o</sup>. 7) this implies the validity of X in any case where  $a > 0$  and  $\beta + \gamma \geq 0$ .

Taking N<sup>o</sup>. 9 into account, we derive from this the validity of X in the case that  $a > 0$  and  $\beta + \gamma < 0$ . For in this case  $-(\beta + \gamma) > 0$ , hence:

$$\begin{aligned} a(\beta + \gamma) &= -a\{-(\beta + \gamma)\} = -a\{-\beta + (-\gamma)\} = \\ &= -\{a(-\beta) + a(-\gamma)\} = -\{-a\beta + (-a\gamma)\} = a\beta + a\gamma. \end{aligned}$$

Consequently X always holds good for  $a > 0$ . From this the validity for  $a < 0$  ensues thus:

$$\begin{aligned} a(\beta + \gamma) &= -(-a)(\beta + \gamma) = -\{(-a)\beta + (-a)\gamma\} = \\ &= -\{-a\beta + (-a\gamma)\} = a\beta + a\gamma. \end{aligned}$$

*Proof of XI.* If  $a$  is a positive real number and if  $a$  and  $b$  are rational numbers satisfying  $0 < a < a, 0 < b < 1$ , we have  $ab < a$ , hence  $ab < a$ . If, inversely,  $c$  is a positive rational number  $< a$  and  $a$  a rational number so that  $c < a < a$ , we have  $c = a \cdot \frac{c}{a}$  where  $0 < a < a$  and  $0 < \frac{c}{a} < 1$ . The set of the numbers  $ab$  ( $a$  and  $b$  rational,  $0 < a < a$ ,



$0 < b < 1$ ), that has  $a.1$  as upper boundary, is, therefore, identical with the set of the positive rational numbers  $< a$ , so that  $a.1 = a$ .

$a.1 = a$  also holds good for  $a = 0$  as in this case both members are 0 and the validity for  $a < 0$  follows from  $a.1 = -\{(-a).1\} = -(-a) = a$ .

*Proof of XII.* If  $a > 0$  and  $\beta > 0$  and if  $a$  and  $b$  are positive rational numbers resp.  $< a$  and  $< \beta$ , we have  $ab \equiv a\beta$  (according to the definition of upper boundary). Consequently from  $ab > 0$  follows  $a\beta > 0$ .

**13. Division of real numbers.** *The possibility and unambiguity of division except by 0, rests on the fundamental properties VII, VIII, IX and XI of N<sup>o</sup>. 12 and*

XIII. *If  $a$  is a given real number different from zero, there is at least one real number  $\xi$  so that  $a\xi = 1$  (possibility of division in 1 except by 0).*

We shall first suppose  $a > 0$ . We represent a rational number  $> a$  by  $a'$ . The set of the numbers  $\frac{1}{a'}$  has an upper boundary (as all

these numbers are  $< \frac{1}{a}$  where  $a$  is a positive rational number  $< a$ );

let this upper boundary be  $\xi$ . If  $a'$  and  $p$  are rational numbers so that  $a' > p > a$ , we have  $\frac{1}{p} \equiv \xi$ , hence  $\frac{1}{a'} < \xi$ . If, inversely,  $b$  is a

positive rational number  $< \xi$ , there exists a rational number  $a'$  so that  $a' > a$  and  $\frac{1}{a'} > b$ ; consequently  $\frac{1}{b} > a'$ , and therefore  $\frac{1}{b} > a$ .

*The set of the positive rational numbers  $< \xi$  is, accordingly, identical with the set of the numbers of the form  $\frac{1}{a'}$  where  $a'$  is rational and*

$> a$ . Consequently  $a\xi$  is the upper boundary of the set of the numbers

$a \cdot \frac{1}{a'} = \frac{a}{a'}$  ( $a$  positive rational and  $< a$ ,  $a'$  rational and  $> a$ ). As

$\frac{a}{a'}$  can assume any positive value  $< 1$  (according to the property of

N<sup>o</sup>. 4), this upper boundary is 1 so that  $a\xi = 1$ , hence  $\xi = \frac{1}{a}$ .

If  $a < 0$  we have  $a \cdot \left(-\frac{1}{-a}\right) = (-a) \cdot \frac{1}{-a} = 1$ , so that XIII is also proved for negative values of  $a$ .

From XIII we find in the known way that  $\frac{\beta}{a} = \beta \cdot \frac{1}{a}$  ( $a \neq 0$ ).

**Physiology.** — *Experiments with JANSEN and DONATH's Antiberiberi-vitamin.* By Prof. Dr. C. EIJKMAN.

(Communicated at the meeting of March 26, 1927).

About thirty years ago I published in the Proceedings of the session of 29 May 1897 a communication from the Medical Laboratory of Weltevreden (Batavia) entitled „The Combating of Beriberi”. It included among other things a report about feeding experiments with gallinaceans, the results of which promised to throw a new light on the etiology of the disease to which so many Orientals succumbed, also in the Dutch Indies.

It had been demonstrated among others by WINKLER, that Beriberi brings on a degeneration of the whole peripheral nervous system, a polyneuritis or rather a polyneuratrophy. The symptoms of the disease tend to the same conclusion.

As to the etiology of the disease, however, researchers were still much in the dark. Truly, various theories had been advanced, but none of them gave satisfaction, for the prophylactic and the curative measures based on them yielded no or only little and temporary success.

At the time it appeared that a one-sided diet of polished rice could produce polyneuritis in gallinaceans, whereas unpolished or undermilled rice, the so-called silverlayer-rice, produced a sheltering as well as a remedial effect.

It has been the great merit of Dr. VORDERMAN, Medical Inspector in Java, that, after having got cognizance of the above-named results, he has instituted a special inquiry into the occurrence of beriberi in the native prisons, in connection with the feeding. It brought to light that in prisons, where polished rice was administered the number of cases of beriberi exceeded about 300 times the number revealed in prisons where unpolished rice was the staple article of diet.

VORDERMAN'S experience has since been corroborated by numerous observations, and even by advisedly undertaken experiments on man, also by researchers out of the Dutch Indies (British India, Japan).

The conclusion I felt confident to deduce from the animal-experiments, continued and extended by GRIJNS after my departure in the same laboratory, was that there must be a substance, or substances in the rice-polishings, responsible for the favourable effect. Indeed, from the polishings an active extract could be obtained that was amenable to further purification. After many vain trials by different researchers it was FUNK, who seemed at length to have succeeded in isolating the

C. EIJKMAN: EXPERIMENTS WITH THE ANTIBERIBERI-VITAMINE OF JANSEN AND DONATH.

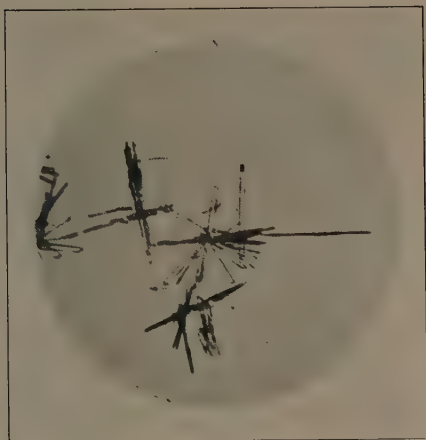


Fig. 1. Crystals of antiberiberi-vitaminchloride.



Fig. 2. Goldddoublesalt.

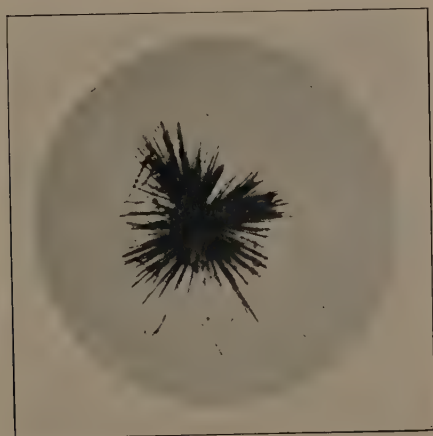


Fig. 3. Vitamin-picrolonate,  
(From JANSEN and DONATH). Enlargement 120  $\times$





active component in a pure, crystalline condition. He imagined it to be an organic nitrogen base of the formula  $C_{17}H_{20}N_2O_7$ . Its administration to an amount of 20 mgrs to pigeons, suffering from polyneuritis, had according to him a rapid curative effect. But afterwards neither he himself nor others have been able to confirm this. Moreover it has been proved that a favourable though only transitory effect can be produced by a number of substances in pigeons suffering from the disease, especially on timely interference, and specially when the substance is given not per os, but subcutaneously. However, these substances have no protective properties.

Meantime the name vitamin that FUNK has given to his substance, has become a generic name. A number of vitamins have now been distinguished, a deficiency of each of which in the diet is supposed to induce as many diseases, the so-called deficiency-diseases or avitaminoses.

Now, it may be called a happy coincidence, that in the same laboratory, where the first researches were made in this field, two of our countrymen JANSEN and his coworker DONATH have apparently succeeded, after many years of persistent endeavours, in isolating the antineuritis or, as they term it, the anti-beriberi vitamin from rice-polishings <sup>1)</sup>.

They report that the addition of as little as 2 mgm., of the vitamin to 1 k.g. of polished rice, ergo in the ratio of 1:500.000, wards off polyneuritis gallinarum. I am in a position to confirm this in virtue of my own experiments with their preparation, to which I shall revert presently. At this rate 1 mgm of vitamin added to  $\frac{1}{2}$  k.g. of polished rice would protect man from an outbreak of beriberi.

Some months back JANSEN and DONATH kindly sent me 40 mgms of their preparation, a white powder, consisting of microscopical needle-shaped crystals (Figs 1—3), well soluble in water, slightly less so in alcohol. The behaviour of the substance towards various reagents used in physiologic chemistry, in connection also with its elementary composition ( $C_6H_{10}ON_2$ ), induces them to think it highly probably, that it contains either an imidazol-, or a pyrimidin-nucleus. The amount of the substance at my disposition being very limited I had to abstain from verifying these reactions. It seemed to me to be more interesting to supplement their experiments by applying the test of FOLIN and DENIS. This test, originally intended for a colorimetric determination of acidum uricum (blue stain with phosphotungstic acid and soda) gives, according to EDDY <sup>2)</sup>, also a positive result with extracts containing the antineuritic vitamin. It now appeared that a 1% solution of the anti-beriberi vitamin yielded with the reagent in question a blue stain, much weaker though than a uric-acid solution of the same concentration.

<sup>1)</sup> These Proceedings Vol. 29, No. 10, 1926. Erratum p. 1392 line 19 from bottom read 3 kg instead of 300 kg.

Geneesk. Tijdschr. v. Ned.-Indië, LXVI afl. 6, 1926.

<sup>2)</sup> Proc. Soc. Exp. Biol. Med. 14, 164, 1917.

Now, in my feeding experiments I had to do without ricebirds, of which the researchers at Weltevreden could avail themselves. These birds yield the advantage that they react rather quickly on a deficiency of the vitamin in question with typical symptoms of polyneuritis, and that, owing to their light bodyweight, they require much less food, consequently also less vitamin than fowls and pigeons, which are generally used for similar experiments. On this account ricebirds were specially adapted to establish the vitamin-content of the various fractions obtained in the isolation-process. Besides, for examining the pure crystalline preparation JANSEN and DONATH have also taken pigeons. Their experiments were exclusively prophylactic, so that they had only to demonstrate that animals on polished rice, to which a certain minimum amount of their vitamin had been added, did not develop polyneuritis, even when they were submitted to a sufficiently prolonged experimentation.

I made curative as well as preventive experiments. According to my experience JANSEN and DONATH's objection, that a number of substances (which certainly do not contain any vitamin) appeared to have a slightly curative effect, applies only to a superficial improvement of short duration, at the most of a few days. The evidence is conclusive, however, when the experiment is continued for a longer space of time and complete recovery is the result. Contrary to them I, therefore, did not desist from curative experiments, especially with a view to their application to man. Fowls yielded hardly any favourable results with such substances. Also in other respects I consider fowls to be in casu first-rate experimental animals, although they require more food than pigeons, which is a drawback. With the latter the symptoms are rather variable. Most often the most conspicuous symptoms at the outset are convulsions and spasms of the neckmuscle, and not, as in cases of beriberi, paresis of the legs. Not rarely, however, do the pigeons succumb unexpectedly without the typical symptoms. As to the behaviour of ricebirds in this respect I must leave it undecided. In fowls the aspect of the disease is more uniform than in pigeons, it reminds us rather of that of beriberi in man, as KUENEN<sup>1)</sup> also maintains. The progress of the disease is slower than in pigeons, so that there is less chance of the animal dying pending the experiment. Another objection raised by JANSEN and DONATH to the use of cocks, is that it often takes months before they manifest symptoms of polyneuritis. My experience is that this is not the case with half-grown cocks, as will be shown by the experiments described lower down, in which the incubation lasted with four cocks, fed on polished rice without vitamin, respectively 21, 23, 24 and 28 days. This, as we shall see, is even a shorter interval of time than the maximum with our pigeons.

Still, in pursuing the line of research of JANSEN and DONATH I first

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<sup>1)</sup> Ned. T. v. Geneesk. 1917 I p. 2091 sqq.

of all experimented with pigeons. Whether the quantity of vitamin left after this, should be sufficient to experiment also with cocks, would appear afterwards.

### *Experiments with pigeons.*

Nine pigeons were divided into three groups, in such a way that the total weight of the several groups inter se was about equal.

*Group I* serves as a test-group. Their trough is filled only with polished rice without vitamin. Bodyweight at the commencement of the experiment, resp. 285, 325, and 450 gms., with an empty crop, total weight 1060 gms.

*Group II* gets polished rice to which 2 mgms of vitamin-hydrochlorid per kg is added. Bodyweight respectively 325, 345 and 375, total weight 1045 gms.

*Group III* gets polished rice with 4 mgrs of vitamin-hydrochlorid per kg. Bodyweight resp. 295, 330 and 395 grms, total weight 1020 grms.

Every Wednesday morning the pigeons were weighed, after the food had been removed from the pen on the previous evening, as a full crop increases the bodyweight rather considerably. All are placed in separate pens.

On Dr. JANSEN's suggestion all the 9 pigeons were given, besides the rice ad libitum, every day (except Sundays) a pap consisting of  $\frac{1}{2}$  gm of meat powder, profusely extracted with water, besides this a few drops of codliver oil some salt-solution and water. The meat for the supply of protein, the oil to prevent xerophthalmia.

JANSEN and DONATH have pointed out that the behaviour of the pigeons fed with rice + vitamin-hydrochlorid, is quite different from that of the pigeons fed with rice alone. The latter practically cease eating the polished rice after a few days, making a mess of their diet, while it looks as if they are rummaging for some grains to their taste, while the others finish their allowance with great relish.

This observation was substantiated by our experiments with pigeons. The pigeons of *Group I* which at first ingested about 20 gms per day, soon began to scatter the rice about and had to be fed forcibly, as they took hardly any food spontaneously. In spite of the forced feeding and a heightened meat-diet their bodyweight diminished steadily. In the second week one of the pigeons of this group has lost its usual energy and brightness, it sits huddled up in its pen, its feathers are ruffled. Already on the 16<sup>th</sup> day unmistakable signs of polyneuritis: spasms and convulsions of the muscles of the neck, paresis of the legs. The bodyweight has diminished from 285 to 215 gms. Now the animal is used for a curative experiment. To this end it is given 0.2 mg of vitamin-hydrochlorid per os. The apparent cures, effected by indifferent substances to which we alluded higher up, occur mostly with subcutaneous injection: So JANSEN and DONATH in following the example of THEILER found, that

even an injection of distilled water into diseased pigeons brought about a regression of the symptoms.

The small amount of vitamin was administered by the mouth at 12 o'clock in the day; at 2 o'clock the symptoms were still worse, but at 4.30 the cramps had ceased altogether. Now a trough with rice of group III (4 mg. of vitamin per kg.) is placed in the cage. Next morning the trough is empty, to all appearance the pigeon is restored to health. When this diet is continued, the appetite keeps good at first, the body-weight rises in the course of 17 days to that at the beginning of the experiment, then remains constant for about a fortnight, and then diminishes slowly, which is not surprising, considering such a prolonged monotonous diet. Then the rice of group II (2 mg. per kg.) is passed into the crop daily. After this curative experiment has been continued for 7 weeks in all, it is discontinued. The bodyweight has now fallen to 210 gm., without new symptoms of polyneuritis manifesting themselves. Subsequently the ordinary mixed pigeon-food; within a few weeks the bodyweight has risen above the initial weight.

It is a well-known fact that pigeons as well as fowls are very particular about alteration of food; they may enjoy their food ever so much at the beginning, in the long run they lose their appetite for a monotonous diet, though it may consist of the best foodstuffs.

At the beginning the other two pigeons of the test-group went the same way as the first, only more slowly, for although they sat huddled up, listless, and with ruffled feathers for more than a week already, no typical symptoms were yet visible on the 30<sup>th</sup> day of the experiment. Seeing that the bodyweight of either of them had fallen considerably in spite of the forced feeding (resp. from 450 to 300 grms and from 325 to 200 grms) and since we were afraid that they should succumb to inanition, a curative experiment was decided on in this stage. They were now given rice of group III (4 mgs per kg.). The result was an immediate recovery of the appetite, greater vitality, and a gradual increase of bodyweight. But after some time they fared worse, just as the first control-pigeon: less appetite, decrease of bodyweight, but polyneuritis did not make its appearance and finally improvement in every respect was brought on by ordinary foodstuffs.

The course of our experiment with the groups II and III differed widely from that with the control-pigeons. It is true, that in the long run their appetite also diminished, but the animals ate sufficiently to keep their bodyweight up to the mark in the 5 weeks that they were fed with vitamin-rice. For the rest they kept in good health. After this they got only polished rice without vitamin. The consequence was that the pigeons of group II revealed the typical symptoms of polyneuritis resp. after 20, 26, and 17 days. They were then submitted to the same curative experiment as the first control-pigeon, which again resulted in complete recovery.



C. EIJKMAN: EXPERIMENTS WITH THE ANTIBERIBERI-VITAMINE OF  
JANSEN AND DONATH.



Fig. 4.  
Cock having been fed for 4 weeks with  
polished rice + 1:500.000 vitaminchloride.



Fig. 5.  
Cock with polyneuritis, after having been  
fed for 23 days with polished rice without  
vitamin. Gets then  $\frac{1}{2}$  mg. vitamin per os.



Fig. 6.  
The same cock as in fig. 5, next day. Gets  
then polished rice + 1:500.000 vitamin-  
chloride.



Fig. 7.  
The same cock as in fig. 6, next day.



The pigeons of group III were more resistant than those of group II, very likely because they could lay up a larger store of vitamin in their organism. After they had been deprived of vitamin for 4 weeks, the experiment was discontinued. Indeed the pigeons were less thriving after that time, and their weight had diminished from 1050 in toto to 760 grms in spite of the forced feeding, but the typical signs of the disease have not appeared.

### *Experiments with cocks.*

After the preceding experiments our store of vitamin had run so short that we had to economize.

*Group I.* Four young cocks serving for control. They get polished rice without vitamin. Bodyweight resp. 1400, 1575, 1735 and 1850.

*Group II.* Two young cocks. They are given polished rice with 2 mg. of vitamin-hydrochlorid per kg. Bodyweight resp. 1525 and 1540 grms. In addition all the 6 cocks were given from the 16<sup>th</sup> experimental day 5 grms of meat-powder, 1 c.c. of codliver oil and some salt-mixture, in the way described in our experiments with pigeons.

Just as the pigeons in the preceding experiments the two groups of cocks show a marked difference in their behaviour with respect to the food, already in the second week. The control-birds eat their rice hardly any more of their own accord, they waste it and have to be forcibly fed. Nevertheless the bodyweight decreases, the crop discharges itself slowly, comb and gills hang loose and are pale. After an incubation of from 3 to 4 weeks, the four control cocks develop the typical paralytic form of polyneuritis. Their total bodyweight amounts to 5710 grms, against 6560 at the outset of the experiment. But for forced feeding the difference would undoubtedly have been considerably greater. The small remainder of our store of vitamin still sufficed to subject the cock that was the first to contract the disease, to the beginning of a curative experiment. On the 23<sup>d</sup> day of the experiment, when the animal had been ill for 2 days,  $\frac{1}{2}$  mgrm vitamin-hydrochlorid was administered per os (fig. 5). An appreciable improvement the next day; the bird is strong enough to stand again, but its gait is still unsteady (fig. 6); then rice of group II (2 mgrs of vitamin per kg) is passed into the crop and the next day the animal is slightly better again (fig. 7). In my wide experience with fowls the same recuperation never occurred spontaneously. I am convinced, that without the vitamin the condition would have deteriorated steadily, and the animal would probably have been dying or would have been dead already on the last named day. It was much to be regretted that, owing to the exhaustion of my supply of vitamin, its administration had to be put a stop to. The cock was then gradually restored to health by supplying yeast and the ordinary poultry food.

The two cocks of group II presented during the experiment quite a

different aspect from that of the control-animals, as had also been the case with the pigeons. They kept thriving, gained in weight although their appetite had diminished a little, forced feeding appeared to be unnecessary; comb and gills of a bright red and full of turgor. Such was their permanent condition until the 18<sup>th</sup> day of the experiment, the day on which the last cock of group I got ill. Thenceforth group II was supplied with rice alone, i. e. without vitamin. It was passed into the crop with 5 grms of meat-powder, 1 cc of codliver-oil etc. With this diet the cocks contracted polyneuritis after resp. 13 and 20 days. The predisposition of these animals to the disease, to which they had previously offered such a stout resistance, as compared with the control-animals, has thus been established. The comparatively brief incubation after deprival of vitamin agrees in this respect with the behaviour of the pigeons of group II. Had our supply of vitamin been sufficient for feeding 4 mgrs per kg of rice to a third group of cocks, just as with the pigeons, the incubation period, after the deprivation of the vitamin would most likely have been longer also here.

All things considered we get an impression, that in the long run a supply of 2 mgrs per kg of polished rice would not suffice to keep up the store of vitamin proper to the healthy animal organism; 4 mgrs seems to be quite sufficient.

We find great satisfaction in stating that our experiments tend to corroborate the highly important results of JANSEN and DONATH's accurate researches. There is no doubt but that their isolated substance has the power to ward off polyneuritis gallinarum. We were able also to demonstrate its remedial power, as was to be expected. The authors have remarked with justice, that one cannot reasonably doubt of the purity of their substance, of which already a wonderfully small dosis yields the desired effect, and which could be isolated in the form of crystals, while the mother-lye proved much less active, I readily admit, that I had come to think (just as others had), that the protection from polyneuritis could not be ascribed to a single substance, but to a combination of two or more substances, notably because in our efforts to purify extracts, acting antineuritically, we ultimately came to a dead stop, where continued purification abolished the remedial action. This conception has been splendidly negated by the two chemico-physiologists of the Medical Laboratory of Wolvehaven.

*Hygienic Institute of the Utrecht University.*



**Physics.** — *On the Heats, resp. Pressures of Evaporation, Sublimation and Melting, also in the Neighbourhood of the Absolute Zero; in Connection with NERNST's So-Called Heat-Theorem. (On the Equation of State of Solid Substances, IV. (Conclusion)).*  
By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated at the meeting of March 26, 1927).

## I. Introduction.

In the first of three papers <sup>1)</sup> I drew up an equation of state for solid substances, which, as regards form, corresponds to that of VAN DER WAALS for liquids and gases. I showed that not only the values of the coefficients of expansion and compressibility, calculated from this equation of state, are in very good harmony with the values found experimentally, but also the coefficients of the pressure and the temperature of this latter coefficient.

In the second paper I derived the relation which, according to a known thermodynamic formula, must exist at high and low temperatures between the second member of the equation of state (the temperature part) and the temperature part of the expression for the *Energy*.

Finally in the third paper the expressions for Energy and Entropy were more closely considered, also at very low temperatures; and the known expression for the Entropy constant in the  $RT$ -region was derived from the value of the so-called elementary volume, in connection with the zero-point energy.

As was already announced on p. 698 of the third paper, it remains reserved for this fourth (concluding) paper to draw up the different equations of the pressure in connection with the different heats of transformation in case of coexistence of liquids resp. solid substances with their vapour, of liquids with solid substances, and of solid substances inter se.

Let us first state that I think I have proved in the third of the papers cited, that the so-called "*energy-degeneration*" at *very low* temperatures, in consequence of which  $RT$  becomes  $A'T^4$ , resp.  $AT^4$  both in the equation of state and in the equation of energy, is found only with *solid* substances, in which the molecules (atoms) move round fixed positions of equilibrium; but that liquids and gases (unless at exceedingly high pressures) remain in the  $RT$ -region down to the lowest temperatures, i.e. do *not* degenerate. For gases this is clear, because there at very low

<sup>1)</sup> These Proc. 29, 95—112, 497—514 and 683—698 (1926).

temperatures the quantity  $\theta$  (the so-called "characteristic" temperature of DEBYE) would approach 0 (cf. p. 684—685 loc. cit.) in consequence of the exceedingly great volume, that is if there could be question of degeneration in gases. And for liquids (with the exception of Helium), which can only exist at higher temperatures (above the melting point), this is, after all, a matter of course.

All the same — even at high temperatures — the assistance of the energy-degeneration has been very often called in (especially in Germany) to account for deviations in liquids, which could of course *not* be explained by the aid of the equation of state of V. D. WAALS with  $a$  and  $b$  constant, but which already found a ready explanation by the assumption of  $b=f(v)$ .

With regard to what has been adduced above, we may point out that PALACIOS MARTINEZ and K. ONNES (Comm. 164, 1923) have shown already before for gaseous  $H_2$  and  $He$ , that even at  $20^{\circ}5$  abs. there is no question as yet of any quantum effect. Besides it was very recently proved by me in two papers <sup>1)</sup>, that also *liquid Helium* does *not* degenerate down to the very lowest temperatures, and that *all* the abnormal phenomena appearing there — e.g. maximum density at  $2^{\circ}3$  abs., minimum density at  $0^{\circ}5$  abs., maximum internal heat of evaporation at  $3^{\circ}4$  abs., minimum *ibid.* at  $1^{\circ}5$  abs., etc. — can be explained in a natural way by the assumption that  $a$  and  $b$  are also functions of the temperature. This latter is, of course, likewise the case for other substances, but there the two decreases with  $T$  *counteract* each other in the equation of state, whereas in Helium  $b$  also decreases, but  $a$  *increases* with  $T$ , on account of the exceedingly low temperatures below the critical temperature ( $5^{\circ}2$  abs.). (c.f. p. 1305 loc. cit., fig. 3).

The formulae for  $a$  and  $b$ , viz.

$$10^6 a = 39,515 + 11,178 T - 1,177 T^2 \text{ (valid to slightly past } T_k) \quad \}$$

$$10^6 b = 1223,4 - 118,45 T + 10,356 T^2 \text{ (valid to } \pm 2^{\circ}3 \text{ abs.)} \quad \}$$

have been derived from known *experimental* data, whereas our considerations concerning  $\lambda$  and  $L$  are further based — besides on this material — on the *experimental* vapour-pressure observations, which go as far down as  $1^{\circ}3$  abs. Hence the *minimum* of  $\lambda$  at  $1^{\circ}5$  has been experimentally established, though the direct confirmation through more accurate measurements of the heat of evaporation  $L$  has at present not yet been extended so far (loc. cit. p. 1333—1334). And as a minimum at  $1^{\circ}5$  abs. is certain ( $\pm 16,5$  gr. cal., cf. p. 1331 loc. cit.), it is clear that  $\lambda$  and  $L$  will approach at  $T=0$  to a slightly greater *finite* limiting value ( $\approx 17,5$  gr. cal.).

This is in contradiction with the opinion of some recent writers, who on the ground of an *erroneous* interpretation of the so-called NERNST-Theorem (which is only valid in the case of coexistence of two

<sup>1)</sup> These Proc. 29, 1303—1316, 1317—1334 (1926).

*solid* phases, and even then only in the neighbourhood of  $T=0$ , see § VI) have come to the conclusion that at  $T=0$  the quantities  $\lambda$  and  $L$  would approach 0 even with the equilibria liquid-vapour (in He) and solid-vapour! <sup>1)</sup>

## II. Equations of state, and expressions for E and S.

We will recapitulate here some formulae, of which repeatedly use will be made in the future. (see in particular the third of the papers cited of 1926, presented to the Academy).

**a. Liquids and gases for all temperatures** (if not at extremely high pressures, see § IV).

$$\left. \begin{aligned} p + \frac{a}{v^2} &= \frac{RT}{v-b} \\ E &= kT + \left( \frac{a_{00}}{v_{00}} - \frac{a}{v} \right) \\ S &= k \log T + R \log (v-b) + S_0 \end{aligned} \right\}$$

For the sake of simplicity it has been assumed here, that  $a$  and  $b$  are no functions of  $T$ , for else a term with  $\frac{db}{dT}$  would have to be added in

$E$ , and  $a - T \frac{da}{dT}$  would have to be substituted for  $a$ . Besides  $b$  has been supposed to be no function of  $v$  either, for else a somewhat more complicated expression would have come in the place of  $\log(v-b)$  in  $S$ . But for our purpose it is perfectly unnecessary to introduce these complications, as we wish to develop only general points of view, which are quite independent of the said complications, which would needlessly render the formulae unmanageable and difficult to survey — only for the sake of a quantitative accuracy unnecessary here.

In the term  $a_{00}/v_{00}$  the limiting volume at  $T=0$ ,  $p=\infty$  is represented by  $v_{00}$ . As at high pressures the quantity  $a$  may possibly be dependent on  $v$ , and at all events dependent on  $T$ , we have written  $a_{00}$  at  $T=0$ ,  $p=\infty$ , and we shall write  $a_0$  at  $T=0$ ,  $p=0$ , to which the volume  $v_0$  corresponds.

For the so-called *Entropy constant*  $S_0$  the following expression is found:

$$\underline{S_0 = -k \log \theta - R \log \omega + k,}$$

<sup>1)</sup> See among others an article by DE KOLOSSOWSKY of Leningrad in the J. de Ch. ph. of Oct. 25, 1926, (23, N<sup>o</sup>. 8), p. 728—732. The writer makes there, nota bene, use of a perfectly wrong formula for  $\frac{dL}{dT} - \frac{L}{T}$ . Compare also my article to refute this in the J. de Ch. ph. of Febr. 25, 1927 (24, N<sup>o</sup>. 2), p. 115—119, and an article by VERSCHAFFELT (Ibid. March 25, 1926 (23, N<sup>o</sup>. 3), p. 238—241) refuting an earlier paper of DE KOLOSSOWSKY (Ibid. 22, 77—79, 1925). To this we may add a still fooler article in the Zeitschr. f. Physik, 43, 509 (Heft 7).

through which the expression for  $S$  becomes *homogeneous*, viz.

$$S = k \log \frac{T}{\theta} + R \log \frac{v-b}{\omega} + k.$$

In this  $\theta$  is the so-called „characteristic” temperature in the solid state at  $v = v_0$  ( $p = 0$ ), and  $\omega$  the so-called “elementary volume”, i.e. the joint volume within the paths which the molecule centres describe round the positions of equilibrium at  $T = 0$  and  $p = 0$  in consequence of the still remaining “zero-point energy”. This in consequence of the alternate action of the mutual attractions and repulsions of molecule nuclei and electrons, which still continues to exist also at  $T = 0$  (zero-point paths). For mon-atomic substances (see my derivation in the third of the papers cited, p. 696)  $\omega$  is represented by ( $k'$  is  $R : N$ ):

$$\omega = \frac{9}{16} \frac{N}{\sqrt{\pi}} \frac{h^3}{(k' \theta)^{3/2} (2\pi m)^{3/2}}.$$

The quantity  $k$  in the expressions for  $S$  and  $S_0$  is everywhere the specific heat at infinitely large constant volume. Its value for mon-atomic substances is  $= \frac{3}{2} R = 3$  gr. cal.

**b. Solid substances at higher temperatures** (if not at extremely high pressures).

$$\left. \begin{aligned} p + \frac{a}{v^2} - \beta &= \frac{RT}{v-b} \\ E &= kT + \left( \frac{a_{00}}{v_{00}} - \frac{a}{v} \right) + P \\ S &= k \log T + R \log (v-b) + S_0 \end{aligned} \right\}.$$

The same remark as above concerning the simplifications with respect to  $a$  and  $b$ .

In the equation of state (see the first of the papers cited) a term  $-\beta$  has now been introduced, which relates to the (static) repulsive virial.

I gave it the form  $\beta = \frac{\lambda/v}{v-b}$ , but this special form is of no consequence for what follows<sup>1)</sup>. The quantity  $P$  in the expression for  $E$  is evidently

$$= \int_v^{\infty} \beta dv.$$

The quantity  $S_0$  has the value indicated above; only the double value  $3R = 6$  gr. cal. (for mon-atomic substances) must now be put for  $k$ , just as in  $kT$  and  $k \log T$  in  $E$  and  $S$ , whereas  $\omega$  has the same value for all the states of aggregation.

<sup>1)</sup> GRÜNEISEN and others assumed the form  $\lambda/vn$ .

### c. Solid substances at very low temperatures.

$$\left. \begin{aligned} p + \frac{a}{v^2} - \beta &= \frac{A'T^4}{v-b} \\ E &= AT^4 + \left( \frac{a_{00}}{v_{00}} - \frac{a}{v} \right) + P + E_0 \\ S &= \frac{4}{3} AT^3 \end{aligned} \right\}.$$

The quantity  $E_0$  is the so-called „zero-point energy” (see above). Further  $A'$  in the equation of state is related to  $A$  in the equation of the Energy (compare for this the second of the papers cited). Both are functions of  $v$ . The variability of  $S$  with the volume, which at higher temperatures was chiefly embodied in the term  $R \log (v-b)$ , has now got into the coefficient  $A$ .

### III. Equilibrium liquid-vapour.

(Above the melting-point; only in Helium down to  $T=0$ ).

If in what follows we always denote the solid state by the index 1, the liquid by 2, and the vapour by 3, the following equation follows immediately from the equalization of the thermodynamic potentials  $Z = E + pV - TS$  of liquid and vapour:

$$(E_3 - E_2) + p(v_3 - v_2) = T(S_3 - S_2), \text{ i.e. } L = T(S_3 - S_2),$$

when  $L = (E_3 - E_2) + p(v_3 - v_2)$  represents the *total* heat of evaporation. Hence we have according to a. of § II, because the limiting values  $a_{00}/v_{00}$  for the smallest volume  $v_{00}$  possible are of course identical for liquid and vapour at  $T=0$ ,  $p=\infty$ :

$$L = (k_3 - k_2) T + \left( \frac{a_2}{v_2} - \frac{a_3}{v_3} \right) + p(v_3 - v_2).$$

But also  $k_2 = k_3$ , because both refer to  $v = \infty$ . Further at comparatively low temperatures (i.e. far enough from the critical temperature, e.g. below the boiling-point) the liquid volume  $v_2$  may be neglected by the side of the vapour volume  $v_3$  (and therefore  $1/v_3$  by the side of  $1/v_2$ ), so that, as  $p v_3 = RT$  may then be put, finally simply

$$L = \frac{a_2}{v_2} + RT \dots \dots \dots (1)$$

is found. In this  $a_2/v_2$  is the *internal* heat of evaporation and  $RT$  the external work.

From  $L = T(S_2 - S_1)$  follows:

$$L = RT \log \frac{v_3 - b_3}{v_2 - b_2} = RT \log \frac{p + a_2/v_2^2}{p + a_3/v_3^2},$$



as  $k_2$  is again  $= k_3$  in  $(k_3 - k_2) \log T$ , and also  $(S_0)_2$  will be  $= (S_0)_3$ , the fraction after the  $\log$ -sign having been transformed by means of the equation of state. At comparatively low temperatures (see above)  $p$  is, however, neglected by the side of  $a_2/v_2^2$ , but for vapour exactly inversely  $a_3/v_3^2$  with respect to  $p$  (in consequence of the great value of  $v_3$ ), so that we get:

$$L = RT \log \frac{a_2/v_2^2}{p} \dots \dots \dots (2)$$

The equation (1) serves to determine  $L$ ; equation (2) for the calculation of  $p$ .

It follows immediately from (1), that at  $T=0$  [this is realizable in Helium; in all other substances only through extrapolation below the melting-point]  $L$  approaches the **finite** value  $a_0/v_0^1$ , in which  $a_0$  and  $v_0$  refer to  $T=0$  and the corresponding vapour pressure  $p=0$ .

From the equating of (1) and (2) follows after division by  $RT$ :

$$\log p = -\frac{a_2/v_2 + RT}{RT} + \log \frac{a_2}{v_2^2} = -\frac{L}{RT} + \log \frac{a_2}{v_2^2}, \dots (3)$$

that is to say at "comparatively" low temperatures, where the above mentioned simplifications are valid. We see that the extrapolated vapour pressure exponentially approaches 0 at  $T=0$ , this also being the case with  $dp/dt$ . The latter follows, indeed, also from  $\frac{dp}{dt} = \frac{L}{T(v_3 - v_2)} = \frac{L}{Tv_3}$ , in which  $v_3$  (exponentially) approaches more strongly to  $\infty$  than  $T$  to 0.

When (3) is written in the form

$$\log p = -\frac{L_0}{RT} + C + DT + \dots = -\frac{a_0/v_0}{RT} + \log \frac{a_0}{v_0^2} - a_0 T \dots (3 \text{ bis})$$

by the expansion of  $a_2/v_2$  and  $\log a_2/v_2^2$  into a series with respect to  $T^2$ ,  $L_0 = a_0/v_0$  can be easily determined from vapour pressure observations, and therefore, if  $v_0$  is known at  $T=0$ ,  $p=0$  by extrapolation, also

1) We saw already in § I that DE KOLOSSOWSKY lately came to the amazing discovery, that also at this equilibrium  $L$  would have to approach 0! In the liquid also the constant of attraction  $a$  would then have to approach 0, which is of course, nonsense. We might communicate more discoveries of this kind; some Italian authors have in view no less than the substitution of an entirely "new" theory of Thermodynamics for the earlier "antiquated" one. Also these authors arrive at the most startling, and (it need hardly be said) the most absurd results!

2) When  $a$  and  $b$  are assumed to be constant, one finds easily by the aid of the equation of state  $\frac{a}{v} = \frac{a_0}{v_0} - RT - x_0 RT^2 \dots$ , in which  $x_0$  is the coefficient of expansion at  $T=0$ , i.e.  $\frac{1}{v_0} \left( \frac{dv}{dT} \right)_0 = \frac{Rv_0}{a}$ . Further  $\log \frac{a}{v^2}$  is then  $= \log \frac{a_0}{v_0^2} - 2x_0 T \dots$

$a_0$  is known, i.e. the *extrapolated* limiting value of  $a_2$  at very low temperatures. In this way the quantity  $a$  has been calculated by me in many cases (also for melted metals and salts, where  $a$  varies very little with the temperature).

If  $b = f(v)$  had been taken into consideration, a term with  $\log T$  would have been added in the second member in (3), and also the vapour pressure constant  $\log a_0/v_0^2$  would have become somewhat more complicated, especially when also  $a$  and  $b$  are considered as functions of  $T$ . But in any case these constants  $C$  at the equilibrium liquid-vapour have nothing whatever to do with the "chemical" constants, introduced by NERNST, which are in relation with the constants of entropy<sup>1)</sup>. In the case  $b = f(v)$  the coefficient of  $\log T$  will always be **negative**, and depend in a simple way on the degree of variability of  $b$  with  $v$ . (Compare also my "Zustandsgl.",

p. 265–278). As  $\frac{dL}{dT}$  is  $=(c_p)_3 - (c_p)_2$ <sup>2)</sup>, i.e.  $L = L_0 + [(c_p)_3 - (c_p)_2]_0 T \dots$ ,

it follows from  $\frac{dp}{dT} = \frac{L}{Tv_3}$  or  $\frac{1}{p} \frac{dp}{dT} = \frac{L}{RT^2}$ , that  $\log p$  will be  $= -\frac{L_0}{RT} +$

$+ \frac{[(c_p)_3 - (c_p)_2]_0}{R} \log T + \text{etc.}$  Now (when  $a$  and  $b$  are no functions of  $T$ )

$(c_p)_3$  is always  $=(c_p)_2$ ; but when  $b = f(v)$ ,  $(c_p)_3$  in the vapour will always be considerably smaller than  $(c_p)_2$  in the liquid, so that the coefficient of  $\log T$   $[(c_p)_3 - (c_p)_2 \text{ at } T=0 \text{ (extrapolated)}]$  differs but little from this quantity at higher temperatures] is always *negative*. Hence never  $= +1.75$ , as NERNST c.s. on the ground of a certain Theorem of Heat, which is absolutely misapplied here, would try to make us believe — even at 4000 to 5000°!

## IV. Equilibrium solid-vapour.

### a. At higher temperatures.

As long as no degeneration of the energy is perceptible in the solid phase, and we are, therefore, still in the  $RT$ -region, there is no essential difference with the equilibrium liquid-vapour. The difference is only, that in the expression (1) for  $L$  (the total *sublimation heat*) a term  $-P_1$  of the (static) repulsive forces is added, according to b. of § II, and  $k_3$  (vapour)  $= \frac{3}{2}R$  for mon-atomic gases will now not be  $= k_1$  (solid)  $= 3R$ . We thus obtain:

$$L = (k_3 - k_1) T + \left( \frac{a_1}{v_1} - P_1 \right) + RT, \quad . \quad . \quad . \quad (1^a)$$

<sup>1)</sup> The vapour-pressure constants  $C = \log a_0/v_0^2$  at  $a$  and  $b$  constant are evidently in relation to the logarithms of the *critical pressures*  $\left( p_k = \frac{1}{27} \lambda \frac{a_k}{b_k^2} \right)$ .

<sup>2)</sup> This formula, too, is only valid at "comparatively" low temperatures. Cf. Zustandsgl. p. 121–123, and the Article in the J. Chim. phys. against DE KOLOSSOWSKY cited in § I.

(2) becoming:

$$L = T \left[ (k_3 - k_1) \log T + R \log \frac{a_1/v_1^2 - \beta_1}{p} + (S_0)_3 - (S_0)_1 \right],$$

which with  $(S_0)_3 - (S_0)_1 = -(k_3 - k_1) \log \theta + (k_3 - k_1)$  according to § II passes into

$$L = T \left[ (k_3 - k_1) \left( 1 + \log \frac{T}{\theta} \right) + R \log \frac{a_1/v_1^2 - \beta_1}{p} \right], \quad . \quad . \quad (2^a)$$

in which  $a_1/v_1^2 - \beta_1$  will now approach 0 at  $T=0$  ( $p=0$ ). For with  $\beta = \frac{\lambda/v}{v-b}$  the equation of state, neglecting  $p$ , becomes  $\frac{a}{v^2} = \frac{\lambda/v + RT}{v-b}$ ;

so that (extrapolated)  $\frac{a}{v^2}$  becomes  $= \frac{\lambda/v}{v-b} = \beta$  at  $T=0$ , i.e.  $a/v^2 - \beta = 0$ .

And since  $\lambda/v$  remains finite at  $T=0$ ,  $p=0$ , this must also necessarily be the case with  $v-b$ . (Not before  $p=\infty$  will  $v$  become  $=b$ ). As the extrapolated value of  $a_1/v_1^2 - \beta_1$  will approach 0 at  $T=0$ ,  $p=0$ , this expression must be replaced by  $RT:(v-b)$  in  $(2^a)$ , in consequence of which we get:

$$\log p = -\frac{L}{RT} + \frac{k_3 - k_1}{R} \left( 1 + \log \frac{T}{\theta} \right) + \log T + \log \frac{R}{v-b}, \quad . \quad (3^a)$$

in which  $L$  is given by  $(1^a)$ , and  $k_3 - k_1$  will be negative. Again both  $p$  and  $dp/dt$  (extrapolated) will approach 0 at  $T=0$ , as  $L_0 = a_0/v_0 - P_0$  remains finite.

Let us write  $(3^a)$  in the form

$$\log p = -\frac{a_1/v_1 - P_1}{RT} + \frac{k_3 - k_1 + R}{R} \log T - \frac{k_3 - k_1 + R}{R} + \frac{k_3 - k_1}{R} (1 - \log \theta) + \log \frac{R}{v-b},$$

as  $(k_3 - k_1) T + RT$  of  $L$ , divided by  $RT$ , yields the constant term  $-(k_3 - k_1 + R):R$ . Hence we get:

$$\log p = -\frac{a_1/v_1 - P_1}{RT} + \frac{k_3 - k_1 + R}{R} \log T + \left[ \log \frac{R}{v-b} - \left( 1 + \frac{k_3 - k_1}{R} \log \theta \right) \right],$$

in which  $a_1/v_1 - P_1$ , expanded into a series with regard to  $T$ , will yield no term with  $T$ , so that  $-$  divided by  $RT$  — no further constant term is to be expected<sup>1)</sup>. Accordingly again no "chemical" constants occurs in

<sup>1)</sup> For from  $\frac{a}{v^2} = \frac{\lambda/v + RT}{v-b}$  follows  $-\frac{2a}{v^3} \frac{dv}{dt} = -\frac{\lambda/v + RT}{(v-b)^2} \frac{dv}{dt} - \frac{\lambda/v^2}{v-b} \frac{dv}{dt} + \frac{R}{v-b}$ , i.e.  $\frac{dv}{dt} \left[ -\frac{2a}{v^3} + \frac{a}{v^2} \frac{1}{v-b} + \frac{\lambda/v^2}{v-b} \right] = \frac{R}{v-b}$ , when  $\frac{a}{v^2} (v-b)$  is put for  $\lambda/v + RT$ . Hence we get  $\frac{dv}{dt} \frac{a}{v^2} \left[ -2 \frac{v-b}{v} + 1 + \frac{\lambda}{a} \right] = R$ . Now according to the equation of state

the vapour-pressure constant  $C$ , no more than in the case liquid-vapour.

If now  $a_1/v_1 - P_1 = (a_0/v_0 - P_0) + \alpha T^2$  (see Note 1) is written, and further  $\log \frac{R}{v-b} = \log \frac{R}{v_0-b_0} + \gamma T$ , in which according to the subjoined Note  $v_0-b_0$  is  $= v_0 \times \frac{\lambda}{a_0}$ , so that  $\log \frac{R}{v_0-b_0}$  becomes  $= \log \left( \frac{R}{v_0} \frac{a_0}{\lambda} \right)$ , we get finally:

$$\log p = - \frac{a_0/v_0 - P_0}{RT} + \frac{k_3 - k_1 + R}{R} \log T + \left[ \log \left( \frac{R}{v_0} \frac{a_0}{\lambda} \right) - \right. \\ \left. - \left( 1 + \frac{k_3 - k_1}{R} \log \theta \right) \right] + DT + \text{etc.} \quad (3^a \text{ bis}).$$

so that the extrapolated limiting value  $L_0 = a_0/v_0 - P_0$  can be calculated from vapour pressure observations. At present  $a_0$  can only be determined, if  $P_0$  should be known.

The coefficient of  $\log T$  agrees with  $dL/dt = k_3 - k_1 + R$  according to (1<sup>a</sup>); which also ensues from  $dL/dt = (c_p)_3 - (c_p)_1 = (k_3 + R) - k_1$ , so that also on integration of  $\frac{d \log p}{dt} = \frac{L}{RT^2}$  a term  $\frac{k_3 - k_1 + R}{R} \log T$  duly occurs.

If  $b$  is still dependent on  $v$  (in solid substances in a much smaller degree than in liquids), some supplementary terms must be added. But in any case the coefficient of  $\log T$  will be *negative* again (in monatomic substances  $= \frac{5}{2}R - 3R = -\frac{1}{2}R$ , or greater negative, when  $b = f(v)$  is assumed); but never  $+1.75$ . For it is entirely disregarded by NERNST and many others, that the expansions into series, holding at *very low* temperatures in the  $T^4$ -region, are *not* valid at *higher* temperatures in the  $RT$ -region, and vice versa. In the intermediate region, where neither of the expansions into series are valid, only the complete DEBYE-formula for  $E$  and  $S$  can be used. The impermissible application of expansions into series, holding only at *very low* temperatures, also at much higher temperatures; and besides the assumption of Energy-degradation also for liquids and gases, have been the two greatest errors of the adherents of the Theorem of Heat.

Besides, it was a serious error of NERNST's to think that *merely* by

evidently  $\frac{v_0-b_0}{v_0}$  is  $= \frac{\lambda}{a}$  at  $T=0$ , so that  $\left( \frac{dv}{dt} \right)_0 = \frac{Rv_0^2}{a} \frac{1}{1-\lambda/a} = \frac{Rv_0^2}{a} \frac{v_0}{b_0}$ . And as

$\frac{1}{v} = \frac{1}{v_0} - \frac{1}{v_0^2} \left( \frac{dv}{dt} \right)_0 T \dots$ ,  $\frac{a}{v}$  becomes  $= \frac{a}{v_0} - \frac{v_0}{b_0} RT$ . Further  $P = P_0 + \left( \frac{dP}{dv} \frac{dv}{dt} \right)_0 T \dots$

which with  $P = \int \frac{\lambda/v}{v-b} dv$ , hence  $\left( \frac{dP}{dv} \right)_0 = - \frac{\lambda/v_0}{v_0-b_0} = - \frac{a}{v_0^2}$ , becomes  $P = P_0 - \frac{v_0}{b_0} RT$ .

For  $\frac{a}{v} - P$  we find, therefore,  $\frac{a_0}{v_0} - P_0 + \text{terms with } T^2 \text{ etc.}$ , but not with  $T$ .

the application of his Theorem of Heat it would be possible to get to know something concerning the vapour pressure constants, i.e. of the integration constant of the equation  $\frac{d \log p}{dt} = \frac{L}{RT^2}$ . He overlooked, that the *direct* calculation of  $\log p$  from the equating of the thermodynamic potentials, which leads to (3) and (3<sup>a</sup>), immediately yields the vapour pressure constant; i.e. it yields the *true* value of this constant <sup>1)</sup>, and not the *wrong* value in consequence of the application of a theorem, which is *not valid* at higher temperatures!

**b. At very low temperatures** (does not occur in Helium).

As soon as there is question of degeneration in the solid phase, the matter is entirely different. According to c. of § II the following equation will be found for  $L$  — that is to say when the  $T^4$ -region is entered:

$$L = \left[ k_3 T + \left( \frac{a_{00}}{v_{00}} - \frac{a_3}{v_3} \right) \right] - \left[ A_1 T^4 + \left( \frac{a_{00}}{v_{00}} - \frac{a_1}{v_1} \right) + P_1 + E_0 \right] + p(v_3 - v_1),$$

in which the first part refers to the vapour. When  $A_1 T^4$  is neglected with respect to  $k_3 T$ ,  $a_3/v_3$  by the side of  $a_1/v_1$ ,  $v_1$  by the side of  $v_3$ , while  $p v_3 = RT$  is put, we find:

$$L = \left( \frac{a_1}{v_1} - P_1 - E_0 \right) + (k_3 + R) T \quad . \quad . \quad . \quad (1^b)$$

The heat of sublimation continues, therefore, to be finite unto  $T=0$ , as then evidently  $L_0 = a_0/v_0 - P_0 - E_0$ .

From  $L = T(S_3 - S_1)$  follows:

$$L = T \left[ \{ k_3 \log T + R \log (v_3 - b_3) + (S_0)_3 \} - \frac{4}{3} A_1 T^3 \right],$$

i.e. when the term with  $T^3$  is neglected, and with  $v_3 - b_3 = v_3 = RT:p$ :

$$L = T \left[ (k_3 + R) \log T - R \log p + R \log R + (S_0)_3 \right]. \quad . \quad . \quad (2^b)$$

And from (1<sup>b</sup>) and (2<sup>b</sup>) follows for  $p$ :

$$\log p = -\frac{L}{RT} + \frac{k_3 + R}{R} \log T + \left( \log R + \frac{(S_0)_3}{R} \right), \quad . \quad . \quad (3^b)$$

which, at  $T=0$ , again gives  $p=0$ ,  $dp/dt=0$ .

The form of the vapour pressure formula has remained the same, but *not until now* has the coefficient of  $\log T$  become *positive*, viz.  $c_p : R$  in the vapour; i.e.  $5/2$  in monatomic vapours,  $7/2$  in diatomic vapours, etc. — but all the same *never*  $+1.75$ , as NERNST c.s. always give.

<sup>1)</sup> When in 1906 NERNST published his first communication in reference to this, I immediately brought forward my objections to his views. The paper had, already, been printed and corrected, when the Editor of the Z. Elektrochem., ABEGG, requested me kindly but urgently, to withdraw my paper, because NERNST had "energetically" protested against its insertion. The corrected Revision of the paper, written Nov. 10 (eingegangen Nov. 22) 1906, has lain in a drawer of my writing-desk for 20 years now.



If for  $L$  its value according to (1<sup>b</sup>) is written, bearing in mind that  $a_1/v_1 - P_1 - E_0$  again does not yield a term with  $T^1$ , we get the following equation, taking into consideration that  $S_0 = -k \log \theta - R \log \omega + k$  (cf. a. of § II):

$$\log p = -\frac{a_0/v_0 - P_0 - E_0}{RT} + \frac{k_3 + R}{R} \log T + \left[ -\frac{k_3 + R}{R} + \log R - \frac{k_3}{R} \log \theta - \log \omega + \frac{k_3}{R} \right] + DT^4 \dots,$$

i.e.

$$\log p = -\frac{a_0/v_0 - P_0 - E_0}{RT} + \frac{k_3 + R}{R} \log T + \left\{ \log \frac{R}{\omega} - \left( 1 + \frac{k_3}{R} \log \theta \right) \right\} + DT^4 + \text{etc.} \quad (3^b \text{ bis})$$

so that only now the vapour pressure constant  $C$  is in connection with the so-called "chemical" constant through  $(S_0)_3$  or  $\omega$ . From vapour-pressure observations (if possible, see below)  $(S_0)_3$  might be determined.

As according to § 2  $\log \omega = \log \omega_0 - \frac{3}{2} \log \theta - \frac{3}{2} \log m$  may be written for  $\log \omega$ , in which, therefore,  $\omega_0$  has the same value for all substances, we may write for  $C$  in monatomic substances  $C = \log \frac{R}{\omega_0} + \frac{3}{2} \log \theta + \frac{3}{2} \log m - 1 - \frac{3}{2} \log \theta, \frac{k_3}{R}$  then being  $= \frac{3}{2}$ .

Accordingly we get in this case:

$$C = \left( \log \frac{R}{\omega_0} - 1 \right) + \frac{3}{2} \log m = C_0 + \frac{3}{2} \log m,$$

in which  $m$  is the atomic weight of the (monatomic) substance. (In multi-atomic substances likewise  $C'$  will be  $= C'_0 + \frac{3}{2} \log m$ , but then  $C'_0$  is not  $= C_0$  in monatomic substances, and besides  $C'_0$  will depend on  $\theta$ , which quantity will be different in every substance).<sup>2)</sup>

If in solid substances at such low temperatures as those at which (3<sup>b</sup> bis) is valid, vapour-pressure observations are possible (the vapour pressures will mostly be so low then, that they are inaccessible to direct measurement; at any rate so far they have not yet been measured

1) Even no terms with  $T^2$  and  $T^3$ , because  $\frac{dv}{dt}$  is now of the order of  $T^3$ , hence  $1/v_0 - 1/v_1$  and  $P - P_0$  of the order of  $T^4$ . (See also the Note in a.).

2) With regard to the homogeneity of the different formulae it may be pointed out, that e.g. in (3<sup>b</sup> bis)  $\omega$  is a volume, hence it has the dimensions  $R\theta : \pi$ .  $\log (R : \omega)$  is therefore of the dimensions  $\log \pi - \log \theta$ , so that we may write  $\log \frac{P}{\pi} = -\frac{a_0/v_0 \text{ etc.}}{RT} + \frac{k_3 + R}{R} \log \frac{T}{\theta} - 1$ , which is perfectly homogeneous.

in any substance), the limiting value  $L_0 = a_0/v_0 - P_0 - E_0$  could be calculated. And since from vapour-pressure observations at higher temperatures (see under a.) the extrapolated value of  $a_0/v_0 - P_0$  can be determined,  $E_0$  could in this way be found experimentally.

## V. Equilibrium solid-liquid.

### a. At higher temperatures.

This occurs with all substances, from the triple point to not too high pressures; and also in *Helium* as continuation of the low-temperature curve.

For the melting-heat  $Q = (E_2 - E_1) + p(v_2 - v_1)$  the following equation is found:

$$Q = (k_2 - k_1) T + \left( \frac{a_1}{v_1} - \frac{a_2}{v_2} - P_1 \right) + p(v_2 - v_1), \quad (4^a)$$

in which  $k_2 - k_1$  is negative.  $Q = T(S_2 - S_1)$  gives further:

$$Q = T \left[ (k_2 - k_1) \log T + R \log \frac{v_2 - b_2}{v_1 - b_1} + (S_0)_2 - (S_0)_1 \right].$$

But  $(S_0)_2 - (S_0)_1 = (k_2 - k_1)(1 - \log \theta)$ , hence we get:

$$Q = T \left[ (k_2 - k_1) \left( 1 + \log \frac{T}{\theta} \right) + R \log \frac{v_2 - b_2}{v_1 - b_1} \right]. \quad (5^a)$$

As in liquids  $v_2 - b_2 = RT : (p + a_2/v_2^2)$  is always greater than  $v_1 - b_1 = RT : (p + a_1/v_1^2 - \beta)$  in the solid phase, because  $a_1$  is much greater than  $a_2$ ,  $v_1$  and  $v_2$  differing only comparatively little, so that even  $a_1/v_1^2 - \beta$  will be  $> a_2/v_2^2$  also if  $v_2$  should be  $< v_1$ ; and as  $T$  soon approaches to a limiting value above or below the triple point (according as  $v_2$  is  $> v_1$  or  $< v_1$ ), the second term of (5<sup>a</sup>) can be slightly greater than the first (negative), and  $Q$  can be small positive. Experimentally comparatively small positive values are actually always found, much smaller than the much greater heats of evaporation and sublimation.

It also follows from (4<sup>a</sup>) that, as also  $a_1/v_1 - P_1$  will always be  $> a_2/v_2$ ,  $Q$  can become small positive. The negative term  $(k_2 - k_1) T$  has little influence on this, no more than  $p(v_2 - v_1)$  for the case that  $v_2$  should be  $< v_1$ , at least at not too high values of the pressure.

But at very high pressures the matter is different. Then in consequence of the characteristic temperature  $\theta$  becoming higher and higher (see the third of the paper cited, p. 683; the expression for  $\theta$  has, in the denominator, the root from the coefficient of compressibility, which will approach 0),  $T/\theta$  becomes smaller and smaller, and as the expansions into series for  $E$  and  $S$  used, holding for comparatively great values of  $T : \theta$ , are no longer valid, and we then enter the  $T^4$ -region, other expressions will have to be substituted for (4<sup>a</sup>) and (5<sup>a</sup>). With very great values of

$p$  it is then, however, not immediately to be seen from the modified equation (4\*), whether  $Q$  can still remain positive with  $v_2 < v_1$ . But it appears with the greatest clearness from  $Q = T(S_2 - S_1) = T({}^{4/3}A_2 T^3 - {}^{4/3}A_1 T^3) = {}^{4/3}(A_2 - A_1) T^4$ , in which  $A_2$  and  $A_1$  are both very small (these quantities have  $\theta_2^3$  resp.  $\theta_1^3$  in the denominator), while  $A_2$  in the liquid (where the high-pressure degradation is not so far advanced as in the solid phase) will always be  $> A_1$ , that  $Q$  always remains small positive; and not before  $p = \infty$ , when  $A_2$  would become  $= A_1$ , does it approach 0.

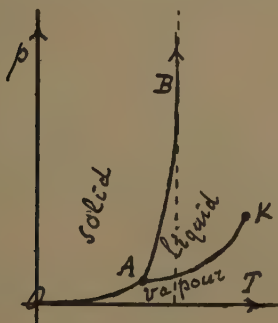
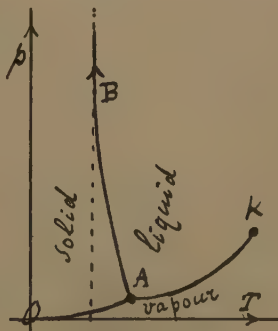
It follows then further from the relation of CLAPEYRON  $\frac{dp}{dt} = \frac{Q}{T(v_2 - v_1)}$ , that with  $v_2 > v_1$  (the most frequently occurring case)  $\frac{dp}{dt}$  will always be positive, and will approach to  $+\infty$  at  $p = \infty$ . For  $Q$  then approaches  $(a_2 - a_1) \frac{T^4}{\theta^3}$ ,  $v_2 - v_1$  approaching to  $(\gamma_2 \sigma_2 - \gamma_1 \sigma_1) \frac{T^4}{\theta^3}$ , in which  $\sigma_2$  and  $\sigma_1$  represent the coefficients of compressibility. For

$$\left(\frac{dv}{dt}\right)_p = \left(\frac{dp}{dt}\right)_v \times -\left(\frac{dv}{dp}\right)_t = \gamma \frac{T^3}{\theta^3} \sigma,$$

because  $A'$  in the equation of state (as regards  $\left(\frac{dp}{dt}\right)_v$ ) has likewise  $\theta^3$  in the denominator, so that  $v = v_0 + \gamma \frac{T^4}{\theta^3} \sigma$ . Hence CLAPEYRON's equation becomes:

$$\frac{dp}{dt} = \frac{a_2 - a_1}{\gamma_2 \sigma_2 - \gamma_1 \sigma_1} \times \frac{1}{T},$$

in which  $T$  remains finite,  $\sigma_2$  and  $\sigma_1$  both verging on 0, so that  $dp/dt$  will approach  $\infty$ , because  $a$  and  $\gamma$  are of the same order of magnitude according to (24) of the second of the papers cited (p. 511).  $Q$  and  $\Delta v$  then approach both 0 at  $p = \infty$ , but  $\Delta v$  (on account of  $\sigma$ ) much more strongly than  $Q$ . In the case  $v_2 > v_1$  the melting-point line has, therefore, a vertical asymptote at a finite value of  $T$  above the triple point.

Fig. 1 ( $v_2 > v_1$ )Fig. 2 ( $v_2 < v_1$ )

If  $v_2 > v_1$  (retrogressive melting-point line),  $\frac{dp}{dt}$  will approach  $-\infty$ , and there will be a vertical asymptote at a temperature below  $A$ .

The case might, however, also present itself, that in the latter case the melting-point line is so strongly retrogressive, or that the triple point is situated so low, that it enters the  $T^4$ -region already at comparatively low, i. e. not too high pressures. Hence not because in  $T: \theta$  the quantity  $\theta$  approaches  $\infty$  at very high pressures at a temperature that remains finite, but because  $T$  itself will approach 0 with  $\theta$  remaining finite. But this case will presently be considered more closely under b.

From (4<sup>a</sup>) follows for  $p$  ( $Q$  is given by (5<sup>a</sup>)):

$$p = \frac{Q - \left( \frac{a_1}{v_1} - \frac{a_2}{v_2} - P_1 \right) + (k_1 - k_2) T}{v_2 - v_1}, \quad \dots \quad (6^a)$$

which will be of the form  $p = -c + \gamma T$  (6<sup>a</sup> bis) with  $v_2 > v_1$ , and of the form  $p = c - \gamma T$  with  $v_2 < v_1$ , i. e. at not too high pressures.

**b. At very low temperatures** (occurs with  $v_2 > v_1$  only for Helium). Though we have already devoted a special article to this case<sup>1)</sup>, we will briefly return to this subject in connection with what we have said above. We now find for  $Q$ :

$$Q = \left[ k_2 T + \left( \frac{a_{00}}{v_{00}} - \frac{a_2}{v_2} \right) \right] - \left[ A_1 T^4 + \left( \frac{a_{00}}{v_{00}} - \frac{a_1}{v_1} \right) + P_1 + E_0 \right] + p(v_2 - v_1),$$

i. e. with neglect of  $A_1 T^4$  with respect  $k_2 T$ :

$$Q = k_2 T + \left( \frac{a_1}{v_1} - \frac{a_2}{v_2} - P_1 - E_0 \right) + p(v_2 - v_1) \quad \dots \quad (4^b)$$

It also follows from  $Q = T(S_2 - S_1)$ , that

$$Q = T \left[ (k_2 \log T + R \log (v_2 - b_2) + (S_0)_2) - \frac{4}{3} A_1 T^3 \right],$$

or with  $v_2 - b_2 = RT: (p + a_2/v_2^2) = RT: a_2/v_2^2$  (because here the comparatively low values of  $p$  can be neglected with regard to  $a_2/v_2^2$ ) and with omission of the term with  $T^4$ :

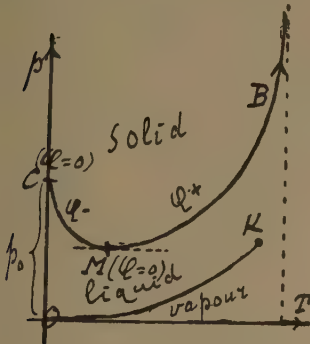
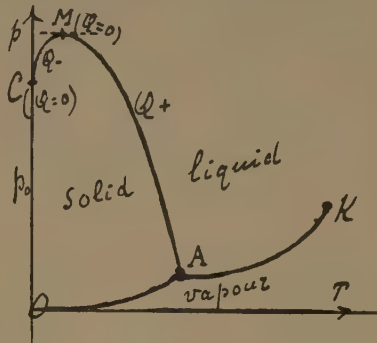
$$Q + T \left[ (k_2 + R) \log T - R \log a_2/v_2^2 + R \log R + (S_0)_2 \right] \quad \dots \quad (5^b)$$

From this follows that at  $T=0$   $Q$  will approach to  $(k_2 + R)T \log T$ , i. e. to  $-0$ . At temperatures somewhat above  $0^\circ$  abs. the *negative* value of  $Q$  will however (in consequence of  $\log T$ ) soon pass through zero, after which it will become and remain *positive*.

Hence it follows from  $\frac{dp}{dt} = \frac{Q}{T(v_2 - v_1)}$ , that at  $T=0$   $\frac{dp}{dt}$  will approach

<sup>1)</sup> These Proc. 30, 244–248 (1927).

$\frac{(k_2 + R) \log T}{v_2 - v_1}$ , i. e. to  $-\infty$  at  $v_2 > v_1$  (Helium; see Fig. 3), and to  $+\infty$  at  $v_2 < v_1$  (retrogressive melting-point lines at low temperatures; see above the conclusion of a. and Fig. 4). The further course will now be at once evident from the two subjoined figures and from (5<sup>b</sup>). The position of the minimum, resp. maximum, at  $M$  will in both cases be given by  $Q = 0$ , i. e.  $(k_2 + R) \log T_m = R \log a_2/v_2^2 - R \log R - (S_0)_2$ .

Fig. 3 (Helium) ( $v_2 > v_1$ )Fig. 4 ( $v_2 < v_1$ )

From (4<sup>b</sup>) follows for  $p$ :

$$p = \frac{Q - k_2 T - \left( \frac{a_1}{v_1} - \frac{a_2}{v_2} - P_1 - E_0 \right)}{v_2 - v_1} - \frac{Q - k_2 T + \frac{r}{v_2} C}{v_2 - v_1}, \quad (6^b)$$

as  $a_1/v_1 - a_2/v_2 - P_1 - E_0$  will be negative owing to  $E_0$ . And as at very low temperatures  $Q = T[k_2 + R) \log T - C']$  according to (5<sup>b</sup>),  $p$  assumes ( $v_2 > v_1$ ) the form

$$p = \alpha T \log T - \beta T + \gamma. \quad (6^b \text{ bis})$$

The latest very interesting observations bij KEESOM<sup>1)</sup> extend only to 1° 2 abs., so that the minimum at about 1° 14 abs. and the subsequent increase of pressure at still lower temperatures (portion MC in Fig. 3) have not yet been confirmed experimentally. But the observations, and the Fig. on p. 1142, lead us to expect a minimum somewhat below 1° 19 with pretty great certainty.

The following values namely have been found.

													(boiling p.) (crit.)
$T$	= 0	0.5	0.7	0.8	0.9	1	1.19	1.42	1.60	1.83			2.04 2.40 2.72 3.12 3.61 4.21 5.19 —
$p_{\text{atm.}}$	= —	—	—	—	—	—	25.3	26.5	27.4	29.8			35.7 48.6 62.8 81.5 108.8 140.5 — —
$p$ (calc.)	54.1	31.0	27.8	26.7	25.7	25.5	25.3	26.1	27.4	29.8			35.7 49.6 63.1 81.5 106.5 140.5 205 —
													(min.)

<sup>1)</sup> These Proc. 29, 1136—1145 (1926).



For the *higher* temperatures from  $2^\circ$  abs. the "calculated" values of  $p$  have been determined according to the formule  $p = -c + \gamma T$  (see (6<sup>a</sup> bis)) above at a.), to which still a term with  $T^2$  has been added, viz.

$$p^{\text{atm.}} = -16,4 + 14,54 T + 5,40 T^2 \text{ (Helium, } 2^\circ \text{ abs. and higher, provided the pressures be not too high).}$$

This formula is in good agreement, but would give entirely wrong results below  $2^\circ$  abs. (gives much too low values for  $p$  then), because then we gradually get into the  $T^4$ -region of the solid state. Then the formula  $p = \alpha T \log T - \beta T + \gamma$  must be used, i.e. in our case:

$$p^{\text{atm.}} = 58,4 T \log^{10} T - 28,6 T + 54,1 \text{ (Helium, below } 2^\circ \text{ abs.)},$$

which formula would yield  $p = 54,1$  atm. at  $T = 0$  ( $dp/dT = -\infty$ ) and presents a minimum at  $T = 1^\circ,14$ , as follows from

$$dp/dT = 58,4 (0,4343 + \log^{10} T) - 28,6 = 58,4 \log^{10} T - 3,24,$$

which is zero at  $\log^{10} T = 0,0554$ ,  $T_{\text{min.}} = 1,136$ , giving  $p_{\text{min.}} = 25,26$  atm. = 25,3 atm.

Experiment will be able to establish an appreciable rise of the pressure not before about  $T = 0^\circ,8$  abs., which will probably increase to more than 50 atm. at  $T = 0^1$ .

*Remark I.* If — what we consider improbable on the ground of several facts (cf. Chapter I) — liquid Helium were degenerated between  $1^\circ,19$  and  $1^\circ,83$ ,  $dp/dT$  would have to decrease in direct ratio to  $T^3$  on decrease of temperature. Now the quantities  $dp/dT$  between  $1^\circ,19$  and  $1^\circ,42$ ,  $1^\circ,42$  and  $1^\circ,60$ , etc. are proportional as  $\frac{0,8}{0,23} : \frac{1,3}{0,18} : \frac{2,4}{0,23}$ , i.e. as 3,2 : 7,2 : 10,5 or as 1 : 2,25 : 3,3, whereas the third powers of the middle temperatures  $1^\circ,305$ ,  $1^\circ,51$ ,  $1^\circ,715$  are in the ratio of 2,22 : 3,44 : 5,04 or as 1 : 1,55 : 2,3. Hence the decrease follows in reality another law, in casu the  $T \log T$ -law, which is valid when the liquid Helium does *not* degenerate.

*Remark II.* According to (5<sup>b</sup>) at  $T = 0$  also  $Q = 0$ , and according to (6<sup>b</sup>)  $p_0$  becomes  $= -\frac{(a_1/v_1 - a_2/v_2) - (P_1 + E_0)}{v_2 - v_1}$ . Now both in the case of  $v_2 > v_1$

<sup>1)</sup> Note added in the English text. In a recent Article (These Proc. 30 (1927)) KEESOM has doubt of the existence of a minimum in the neighbourhood of  $1^\circ$  abs. (or a little lower, for it is very good possible that at that temperature we are still not entirely entered in the  $T^4$ -region), and believes that  $\frac{dp}{dT}$  will approach to 0 at  $T = 0$ . But I think, one cannot conclude this with some certainty from his Figure on the page 1142 l.c. All things are still possible, and a decision will be reserved to further experiments.

I still remark, that KEESOM has calculated the coefficients of my formula (6<sup>b</sup> bis) from experimental data at  $1^\circ,2$ ,  $1^\circ,8$  and  $2^\circ,4$  abs. and has — of course — found no agreement (see the Fig. 2 in his recent Article). For this formula is only valid at *very low* temperatures; for Helium certainly not higher than  $1^\circ,8$ , so that his coefficients are entirely wrong and must be substituted by those, given above.

and of  $v_2 < v_1$   $p_0$  is positive. In the first case the numerator must be negative, in the second case, however, positive. This can only be accounted for, when we assume that  $-a_1$  being greater than  $a_2$  — in the first case (Helium)  $a_1/v_1 - a_2/v_2$  yet remains smaller than  $P_1 + E_0$ ; whereas in the second case  $P_1 + E_0 < a_1/v_1 - a_2/v_2$ .

## VI. Equilibrium between two solid phases.

Here for the first time — in consequence of the degeneration as regards the thermic energy of *both* the phases at very low temperatures — we meet with something, that can be brought in connection with a "Theorem of Heat". But we prefer, also here, to speak of the  $T^4$ -law of DEBYE, according to which  $Q/T$  becomes  $= 0$  at  $T = 0$ , and accordingly the line of equilibrium will present a *horizontal tangent* at C.

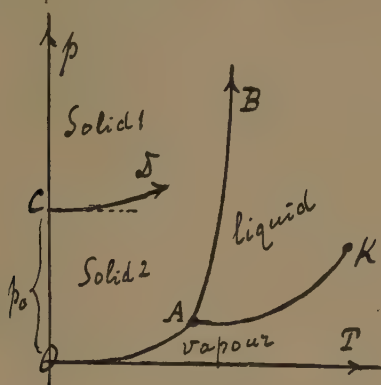


Fig. 5

a. At higher temperatures (e.g. at D).

We then find for  $Q$  at the transition  $1 \rightarrow 2$ :

$$Q = (k_2 - k_1) T + \left[ \left( \frac{a_1}{v_1} - \frac{a_2}{v_2} \right) - (P_1 - P_2) \right] + p(v_2 - v_1), \quad (7^a)$$

and also

$$Q = T \left[ (k_2 - k_1) \log T + R \log \frac{v_2 - b_2}{v_1 - b_1} \right] + (S_0)_2 - (S_0)_1, \quad (8^a)$$

the course of  $p$  along the transformation line according to (7<sup>a</sup>) being determined by

$$p = \frac{Q - (k_2 - k_1) T - \left[ \left( \frac{a_1}{v_1} - \frac{a_2}{v_2} \right) - (P_1 - P_2) \right]}{v_2 - v_1}, \quad (9^a)$$

in which  $Q$  is given by (8<sup>a</sup>). From  $\frac{dp}{dT} = \frac{Q}{T(v_2 - v_1)}$  follows, that  $p$  is ascending or descending according as  $Q$  and  $\Delta v$  have equal or opposite signs. We shall, however, see presently that only the first case will occur.

**b. At very low temperatures** (e.g. in the neighbourhood of C).

In this case we have:

$$Q = (A_2 - A_1)T^4 + \left[ \left( \frac{a_1}{v_1} - \frac{a_2}{v_2} \right) - (P_1 - P_2) - \{ (E_0)_1 - (E_0)_2 \} \right] + p(v_2 - v_1), \quad (7^b)$$

and also

$$Q = \frac{1}{3} (A_2 - A_1) T^4, \quad . . . . . (8^b)$$

so that now  $Q$  will approach 0 proportionally to  $T^4$ , hence  $Q/T \therefore T^3$ , in consequence of which in this special case (equilibrium between two solid phases)  $\frac{dp}{dT}$  will approach 0, since  $v_2 - v_1$  remains finite to the end.

There is, therefore, a horizontal tangent at C.

We find for  $p$ :

$$p = \frac{\frac{1}{3} (A_2 - A_1) T^4 - [ \quad ]}{v_2 - v_1} . . . . . (9^b)$$

According to the formula of CLAPEYRON the pressure will again be ascending or descending, according as  $Q$  (i.e.  $A_2 - A_1$ ) and  $v_2 - v_1$  have the same or opposite signs. Now  $A = \frac{3}{5} R \pi^4 : \theta^3$ , in which  $\theta$  (cf. equation (24) in the second of the papers cited) is proportional to  $v^{-5/2}$ . In consequence of this  $A$  will be  $\therefore v^{5/2}$ , and thus  $A_2 - A_1$  and  $v_2 - v_1$  will always possess the same sign, so that the line of transformation will always be an *ascending* one. (See Fig. 5).

As at  $T = 0$  in Fig. 5 we have assumed  $p_0$  positive, necessarily again according to  $(9^b)$   $(a_1/v_1 - a_2/v_2) - (P_1 - P_2) - ((E_0)_1 - (E_0)_2)$  and  $v_2 - v_1$  will have to possess opposite signs. In Fig. 5  $v_2$  (under lower pressure) is probably  $> v_1$ , hence  $(a_1/v_1 - a_2/v_2) - \text{etc.}$  negative (see also the conclusion of § V under b.).

And now all possible cases of lines of equilibrium between gaseous, liquid and solid phases have been treated. The NERNST-theorem is nowhere to be found, except at the equilibrium between two solid phases, and then only at very low temperatures. The transference of the formulae holding at these temperatures to higher temperatures, as e.g. NERNST does in the case of the two sulphur modifications at  $\pm 100^\circ \text{C.}$  ( $273^\circ \text{abs.}$ ), is absolutely impermissible, for these formulae are no longer valid then. Nor is it permissible to write  $+1.75 \log T$  at higher temperatures in the vapour-pressure formulae, the coefficient for  $\log T$  always being evidently *negative* then! (See § III and IV). Even at very low temperatures the coefficient mentioned is only positive at the equilibrium solid-vapour, and even then never  $+1.75$ , but at least  $+2.5$  (in monatomic substances).

*Tavel sur Clarens (Suisse), Febr.-March 1927.*

**Chemistry.** — *Equilibria in systems, in which phases, separated by a semi-permeable membrane.* XX. By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of March 26, 1927).

*Influence of the pressure on osmotic systems and on the osmotic pressure.*

An osmotic equilibrium, in which  $d$  diffusing substances, and in which occur at the one side of the membrane  $n_1$  components in  $r_1$  phases and at the other side  $n_2$  components in  $r_2$  phases, has, as we have seen in Communication VII, at constant temperature

$$n_1 + n_2 - (r_1 + r_2) + 2 - d$$

licences. Consequently an osmotic equilibrium with one diffusing substance has:

$$n_1 + n_2 - (r_1 + r_2) + 1$$

licences. As at constant temperature the equilibrium at the one side of the membrane has  $n_1 - r_1 + 1$  licences and that at the other side has  $n_2 - r_2 + 1$  licences, we can also say, therefore, that the number of licences at constant temperature is one smaller than the sum of the licences of the two systems.

We now take a system  $E$ , the composition of which we further keep constant; under given pressure the phases of this system are completely defined; they have viz. such composition that the total  $\zeta$  of the system under that given  $P$  (and  $T$ ) is a minimum. The system  $E$  is invariant under given pressure, therefore, so that it has one licence, if the pressure can change also.

If we take now an osmotic equilibrium:

$$(E_1)_{P_1} \mid (E_2)_{P_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which both systems have a constant composition, then this has, in accordance with the membrane-phase-rule above-mentioned:  $1 + 1 - 1 = 1$  licence. If we put still one condition, f.i. that the pressure must be equal on both sides of the membrane, so that we get the osmotic equilibrium:

$$(E_1)_P \mid (E_2)_P \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

then this has no more licence; therefore; it can only exist under a definite pressure  $P$ .

As system (1) has one licence only,  $P_1$  and  $P_2$  are dependent on one another; consequently we can choose only one of those pressures

arbitrarily. With every definite pressure  $P_1$  at the one side of the membrane, a definite other pressure  $P_2$  at the other side is corresponding, therefore; if  $P_1$  increases with a definite value  $dP_1$ , then  $P_2$  must increase with a definite other value  $dP_2$ . Between those increments a relation exists, which we can find as follows. If (1) passes into the osmotic equilibrium:

$$(E_1)_{P_1+dP_1} \mid (E_2)_{P_2+dP_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

then the *O.W.A.* of both systems increases with:

$$d\xi_1 = -\Delta V_{E_1} \cdot dP_1 \quad d\xi_2 = -\Delta V_{E_2} \cdot dP_2 \quad . \quad . \quad . \quad (4)$$

As, however, the *O.W.A.* must remain the same on both sides of the membrane, it follows:

$$\Delta V_{E_1} \cdot dP_1 = \Delta V_{E_2} \cdot dP_2 \quad \frac{dP_2}{dP_1} = \frac{\Delta V_{E_1}}{\Delta V_{E_2}} \quad . \quad . \quad . \quad (5)$$

If  $\Delta V_{E_1}$  and  $\Delta V_{E_2}$  have the same (opposite) sign, then we must, in order to keep both systems in osmotic equilibrium with one another, change the pressure on both sides of the membrane in the same (opposite) direction.

If we draw in a system of coordinates the pressure  $P_1$  on one of the axes and on the other axis the corresponding pressure  $P_2$ , then we have a  $P_1 P_2$  curve, the direction of which is defined in every point by (5). If in a point  $\Delta V_{E_1} = 0$ , then the curve is in this point parallel to the  $P$ -axis; with a small change in pressure of system  $E_1$  we must keep constant then the pressure of the system  $E_2$ .

If we draw in this diagram a straight line, which makes equal angles with the two axes, then the points of intersection of this line with the  $P_1 P_2$  curve represent the pressure  $P$ , under which the osmotic equilibrium (2) exists.

In the special case that  $E_1$  and  $E_2$  represent two gases or vapours, which follow the gas-laws, (5) passes into:

$$\frac{dP_2}{dP_1} = \frac{V_1}{V_2} = \frac{P_2}{P_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

in which  $V_1$  and  $V_2$  represent the molecular volumina of those gases; hence follows:

$$P_2 = C P_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

in which  $C$  is a constant. In order to keep both gases in osmotic equilibrium with one another, we have to change therefore, the two pressures in such a way, that their ratio remains constant. Then the  $P_1 P_2$  curve is a straight line.

If we have chosen the composition of the two vapours in such a way, that they have the same *O.W.A.* under a certain pressure  $P_0$ , then they have it also under every other pressure. Then the constant  $C$  in (7) is 1; the equilibrium (2) then exists not only under a single  $P$ ,



but under all pressures  $P$ . This is the case when both vapours have a same amount of water.

We now take the osmotic equilibrium:

$$(water)_{P_0} \mid E_P \dots \dots \dots (8)$$

in which at the left of the membrane pure water in liquid state under the pressure  $P_0$  and at the right of the membrane an arbitrary system  $E$  under the pressure  $P$ . As  $\pi = P - P_0$  represents the osmotic pressure of the system  $E$  with respect to water under the pressure  $P_0$ , we shall write for (8):

$$(water)_{P_0} \mid E_{P_0+\pi} \dots \dots \dots (9)$$

If we represent the molecular volume of the water under the pressure  $P_0$  by  $v_0$ , then follows from (4):

$$d\xi_0 \doteq -v_0 \cdot dP_0 \dots (10^a) \quad d\xi = -\Delta V_E \cdot dP \dots (10^b)$$

Consequently we find for the osmotic equilibrium (8):

$$v_0 dP_0 = \Delta V_E \cdot dP \quad dP = \frac{v_0}{\Delta V_E} \cdot dP_0 \dots (11)$$

As  $d\pi = dP - dP_0$  follows from (11):

$$d\pi = \left( \frac{v_0}{\Delta V_E} - 1 \right) dP_0 \dots \dots \dots (12)$$

The osmotic pressure of an arbitrary system  $E$  is dependent, therefore, on the pressure  $P_0$  under which the water is; (12) defines the change  $d\pi$  of the osmotic pressure at a small change  $dP_0$  of the pressure of the water. In formula (13) of Communication I we have deduced already this formula (12) in a somewhat other form for the special case that the system  $E$  consists only of one binary liquid.

If we replace in (8) and (9) the water by water-vapour, then we get the osmotic equilibrium:

$$(watervapour)_{P_0} \mid E_P \quad (watervapour)_{P_0} \mid E_{P_0+\pi} \dots (13)$$

in which  $\pi$  now represents the osmotic pressure of the system  $E$  with respect to watervapour of the pressure  $P_0$ . The change of the O.W.A., of the osmotic pressure, etc. is also defined by (10)–(12). However, in this we have to replace the volume  $v_0$  of the water by the volume  $V_0$  of the vapour.

In order to apply the previous considerations to a definite system  $E$  we must know, therefore,  $\Delta V_E$ . If we take for  $E$  one of the equilibria:

$$\left. \begin{array}{ll} (Y + L_w)_P & \text{fig. 1. III} \\ (X + Y + L_c)_P & \text{fig. 1. V} \end{array} \right\} \quad \left. \begin{array}{ll} (Y + L_a)_P & \text{fig. 1. III} \\ (Y + H + L_d)_P & \text{fig. 2. V} \end{array} \right\} (14)$$

etc. which we have discussed in the previous communication, then  $\Delta V_E$  is defined for those systems by the formula's (10<sup>a</sup>), (27), (35) or (38) of the previous communication. As we have formerly seen, it depends on the values of the volumina, concentrations etc. whether  $\Delta V_E$  will be under a definite pressure positive, negative or casually zero. As the magnitudes which define  $\Delta V_E$  are dependent on the pressure,  $\Delta V_E$ , therefore, is also a function of the pressure; consequently it is possible that  $\Delta V_E$  changes its sign with change of pressure.

If we substitute the values, above-mentioned, of  $\Delta V_E$  in (10<sup>a</sup>)—(12) then the change of the O.W.A. and that of the osmotic pressure of the systems (14) is defined.

We now take the osmotic equilibrium (8) or (9) in which  $E$  represents an arbitrary system f.i. one of the systems (14). As  $v_0$  is positive, three cases can occur, viz. under the considered pressures is  $\Delta V_E$ :

- I. positive and larger than  $v_0$ ;
- II. positive and smaller than  $v_0$ ;
- III. negative.

Further we have their mutual combinations and transitions between I and II and between II and III; a transition between I and III is only possible through the medium of II.

In order to represent graphically the further deductions, we take two axes; on the one we draw the pressure  $P_0$  of the water, on the other the osmotic pressure  $\pi$  of the system  $E$  belonging to this pressure  $P_0$ . As to every pressure  $P_0$  belongs an osmotic pressure  $\pi$ , we get, therefore, a  $P_0\pi$ -curve, as f.i. curve  $aegk$  in fig. 1. If the water has f.i. the

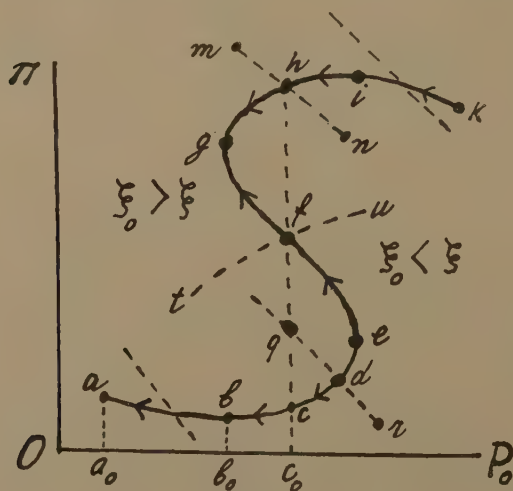


Fig. 1.

pressure  $P_0 = O a_0$ , then system  $E$  has an osmotic pressure  $\pi = a_0 a$  and consequently a total pressure  $P = O a_0 + a_0 a$ .

We now shall consider more in detail the cases, above-mentioned.

I. If we change the pressure of the water with  $dP_0$  then the changes  $dP$  and  $d\pi$  of the total and osmotic pressure of the system  $E$  are defined by:

$$dP = \frac{v_0}{\Delta V_E} \cdot dP_0 \quad . \quad . \quad (15^a) \quad d\pi = - \left( 1 - \frac{v_0}{\Delta V_E} \right) dP_0 \quad . \quad . \quad (15^b)$$

in which the term between parentheses is positive and smaller than 1. If we raise the pressure  $P_0$  of the water, then it appears that the total pressure  $P$  of the system  $E$  becomes larger also, but that its osmotic pressure becomes smaller. Further it is apparent that as well the increase of the total pressure as the decrease of the osmotic pressure, is smaller than the change of pressure which we give to the water. Consequently we get a  $P_0\pi$ -curve as branch  $ab$  or  $ik$  (fig. 1) the first of which is convex to the abscis and the second concave to the abscis.

In fig. 1 are drawn some dotted lines, which make an angle of  $45^\circ$  with the  $P_0$ -axis (in the following viz. we indicate only the angles, smaller than  $90^\circ$ ). It follows from  $(15^b)$  that the tangent in every point of branches  $ab$  and  $ik$  makes with the  $P_0$ -axis an angle smaller than  $45^\circ$ . If we go along branch  $ab$  from  $a$  towards  $b$ , then this is situated, therefore, firstly below and afterwards above the dotted line, which is drawn through a point of this branch; the same is valid for the branch  $ik$ .

As in an osmotic equilibrium the O.W.A. is the same on both sides of the membrane, we can call this the O.W.A. of this equilibrium. The change of this O.W.A., when an osmotic equilibrium goes along branch  $ab$  or  $ik$ , is defined by  $(10^a)$  or  $(10^b)$ . It follows from  $(10^a)$  that the O.W.A. increases with decreasing values of  $P_0$ ; consequently the arrows on  $ab$  and  $ik$  indicate the direction, in which the O.W.A. increases.

If we represent the osmotic equilibria, which are indicated by the points  $a$  and  $b$  by:

$$(water \mid E)_a \quad (water \mid E)_b \quad \text{fig. 1} \quad . \quad . \quad . \quad (16)$$

then is in the first equilibrium:

- the pressure  $P_0$  of the water smaller,
- the osmotic pressure  $\pi$  of system  $E$  larger,
- the total pressure  $P$  of the system  $E$  smaller,
- and the O.W.A. larger than in the second equilibrium.

II. In the case, mentioned sub II the coefficient of  $dP_0$  in the two equations:

$$dP = \frac{v_0}{\Delta V_E} \cdot dP_0 \quad . \quad . \quad (17^a) \quad d\pi = \left( \frac{v_0}{\Delta V_E} - 1 \right) dP_0 \quad . \quad . \quad (17^b)$$

is positive; in (17<sup>a</sup>) this coefficient is larger than 1, in (17<sup>b</sup>) this can be as well larger as smaller than 1. If we raise the pressure  $P_0$  of the water, then the total and the osmotic pressure of the system increases, therefore. The change  $dP$  of the total pressure is larger, the change  $d\pi$  of the osmotic pressure can be greater also, but also smaller than the change  $dP_0$ , which we give to the pressure of the water.

Consequently in a  $P_0\pi$ -diagram we get a curve, as branch  $be$  or  $gi$  in fig. 1. The angle, which makes a tangent to those branches with the  $P_0$ -axis can be as well larger as smaller than  $45^\circ$ .

With the aid of (10<sup>a</sup>) we find again, that the O.W.A. increases along those branches in the direction of the arrows.

III. We now put  $\Delta V_E = -\Delta$ , so that  $\Delta$  is positive. The change of the total and of the osmotic pressure are defined by:

$$dP = -\frac{v_0}{\Delta} \cdot dP_0 \quad d\pi = -\left(\frac{v_0}{\Delta} + 1\right) dP_0 \quad . \quad . \quad . \quad (18)$$

in which the term between parentheses is positive and larger than 1. Just as in the case, discussed sub I, the osmotic pressure decreases with increasing values of  $P_0$ ; in contradiction with I, however, this decrease now is larger than the increase of pressure  $dP_0$  which we give to the water; also the total pressure  $P$  of the system  $E$  decreases with increasing values of  $P_0$ .

Hence follows that now we get a  $P_0\pi$ -curve, as branch  $eg$  which has a falling direction at increasing values of  $P_0$  just as  $ab$  and  $ik$ . In contradiction with the branches  $ab$  and  $ik$  the tangent in every point of this curve  $eg$  makes, however, an angle, which is greater than  $45^\circ$ .

It follows from (10<sup>a</sup>) that the O.W.A. increases along this branch  $eg$  in the direction of the arrows.

IV. With the transition of I into II becomes  $\Delta V_E = v_0$ ; we then get at first approximation:

$$dP = dP_0 \quad d\pi = 0 \quad . \quad . \quad . \quad . \quad . \quad (19)$$

In point  $b$ , where the branches  $ab$  and  $eb$  pass into one another, and in the point  $i$ , where this is the case with the branches  $gi$  and  $ki$ , the tangent is horizontal, therefore. Consequently a small change in pressure  $dP_0$  of the water at first approximation has no influence on the osmotic pressure of the system  $E$ ; this is a minimum then (point  $b$ ) or a maximum (point  $i$ ).

In order to examine this more in detail, we take in (10<sup>a</sup>) and (10<sup>b</sup>) still terms of the second order; then we get:

$$d\xi_0 = -v_0 dP_0 + \alpha_0 dP_0^2 \quad d\xi = -\Delta V_E dP + \alpha dP^2 \quad . \quad . \quad . \quad (20)$$

As those changes of the O.W.A. on both sides of the membrane must be equal, follows:

$$-v_0 dP_0 + \alpha_0 dP_0^2 = -\Delta V_E dP + \alpha dP^2 \quad . \quad . \quad . \quad (21)$$

If we put in this  $\Delta V_E = v_0$  and  $dP = dP_0 + d\pi$  then follows:

$$d\pi = \frac{\alpha - \alpha_0}{v_0} \cdot dP_0^2 : \dots \dots \dots (22)$$

in which the terms, which are infinitely small with respect to those, already written, are omitted. Hence is apparent that the osmotic pressure for  $\alpha > \alpha_0$  is a minimum and for  $\alpha < \alpha_0$  a maximum; also it appears that the curve is parabolic in the vicinity of  $b$  and  $i$ .

The change of the *O.W.A.* has nothing particular in those points  $b$  and  $i$ .

V. With the transition of II into III becomes  $\Delta V_E = 0$ ; then follows from (11) and (12)

$$dP = \infty \quad d\pi = \infty \quad \dots \dots \dots (23)$$

so that the tangent in the points  $e$  and  $g$  is vertical. As  $\Delta V_E = 0$ , we write for (20) and (21):

$$\left. \begin{aligned} d\xi_0 &= -v_0 dP_0 & d\xi &= \beta \cdot dP^2 \\ & & -v_0 dP_0 &= \beta \cdot dP^2 \end{aligned} \right\} \dots \dots \dots (24)$$

If we put  $dP = dP_0 + d\pi$  then we find:

$$d\xi_0 = d\xi = \beta \cdot d\pi^2 \quad \dots \quad (25^a) \quad d\pi = \pm \sqrt{-\frac{v_0}{\beta} \cdot dP_0} \quad (25^b)$$

in which the terms, which are infinitely small with respect to those, already written, are omitted. We now distinguish two cases.

If  $\beta$  is negative, then we can satisfy (25<sup>b</sup>) only by positive values of  $dP_0$ ; with every positive increase of  $dP_0$  then are corresponding a same increase and decrease of the osmotic pressure. Then the curve is situated as in point  $g$ , viz. at the right side of the vertical tangent going through this point. In accordance with the arrows follows from (25<sup>a</sup>), that the *O.W.A.* decreases along this curve starting from point  $g$  in both directions.

The osmotic equilibrium has, therefore, in point  $g$  a minimum-pressure of the water, while the osmotic pressure is maximum.

If  $\beta$  is positive, then we can only satisfy (25<sup>b</sup>) by negative values of  $dP_0$ ; then the curve is situated as in point  $e$ , viz. at the left of the vertical tangent going through this point.

Consequently the osmotic equilibrium gets in the point  $e$  a maximum-pressure of the water, while its osmotic pressure is a minimum.

Further it appears from (25<sup>b</sup>) that the curve is parabolic in the vicinity of the points  $e$  and  $g$ .

The vertical line  $c_0 h$  intersects the  $P_0 \pi$ -curves in three points, which represent the osmotic equilibria:

$$(water \mid E)_e \quad (water \mid E)_f \quad (water \mid E)_h \quad \text{fig. 1.} \quad \dots \quad (26)$$

as, although their osmotic pressures are different, those equilibria yet exist under the same pressure  $P_0 = O c_0$  of the water, they have, therefore, also the same *O.W.A.* In general it follows from this: osmotic equilibria, which are situated in the  $P_0 \pi$ -diagram on a same vertical line have the same *O.W.A.*





an osmotic equilibrium, so that water must diffuse from the one side of the membrane towards the other. In order to define the direction of this diffusion, we have to compare the *O. W. A.* of the water with that of the system *E*; we represent the first by  $\xi_0(q)$  and the second by  $\xi(q)$ .

As the water has the same pressure  $P_0 = O c_0$  as well in the osmotic system (*q*) as in the osmotic equilibrium (*c*), the *O. W. A.* of the water is also the same, therefore, in both systems; consequently we have  $\xi(q) = \xi_0(c)$ . As, however, *c* is an osmotic equilibrium, so that the *O. W. A.* is equal on both sides of the membrane, we have also, therefore,  $\xi_0(c) = \xi(c)$ ; consequently we have:

$$\xi(q) = \xi_0(c) = \xi(c) \quad \text{fig. 1} \quad (32)$$

We now compare the osmotic system (*q*) with the osmotic equilibrium (*d*). As the line *q d* makes an angle of  $45^\circ$  with the  $P_0$ -axis is:

$$O c_0 + c_0 q = O d_0 + d_0 d \quad \text{fig. 1} \quad (33)$$

This means that *E* has the same pressure *P* and consequently also the same *O. W. A.*, as well in the osmotic system (*q*) as in the osmotic equilibrium (*d*). Consequently we have:

$$\xi(q) = \xi(d) = \xi_0(d) \quad \text{fig. 1} \quad (34)$$

It is apparent from the direction of the arrows in fig. 1 that  $\xi_0(c) = \xi(c)$  is greater than  $\xi_0(d) = \xi(d)$ . It now follows from (32) and (33):

$$\xi_0(q) > \xi(q) \quad \text{fig. 1} \quad (35)$$

This means that in the osmotic system (*q*) the *O. W. A.* of the water is larger than that of the system *E*. Instead of (31) we write, therefore:

$$(water \leftarrow E)_q \quad \text{fig. 1} \quad (36)$$

in which the arrow indicates the direction, in which the water diffuses. We find the same for the osmotic systems (*m*) and (*t*).

In the same way as above we find that the water in the osmotic system:

$$(water \rightarrow E)_r \quad \text{fig. 1} \quad (37)$$

must diffuse in the direction of the arrow; this is valid also for the osmotic systems (*n*) and (*u*).

In order to define more in detail the different behaviour of the systems (*q*) and (*r*) we place ourselves in fig. 1 in the point *O* and we consider the lines, which make an angle of  $45^\circ$  with the  $P_0$ -axis. Then *q* is situated on the line *q d r* at the left of the point *d* and *r* is at the right; on the line *m h n* is situated *m* at the left and *n* at the right of the point *h*; etc. Therefore the  $P_0 \pi$ -curve divides the diagram into two parts, of which we shall say that the one is situated at the left and the other at the right side of this curve.

We can summarise the previous results in the following way.

If the osmotic system

$$(water)_{P_0} \mid E_P \quad \text{fig. 1} \quad (38)$$

is represented in the diagram:

1. by a point of the  $P_0\pi$ -curve, then is  $\xi_0 = \xi$ ; then it is an osmotic equilibrium with the osmotic pressure  $\pi = P - P_0$ .

2. by a point at the right side of the  $P_0\pi$ -curve, then is  $\xi_0 < \xi$ ; then it is not an osmotic equilibrium but an osmotic system, in which the water diffuses towards the system  $E$ .

3. by a point at the left of the  $P_0\pi$ -curve, then is  $\xi_0 > \xi$ ; then the water diffuses away from system  $E$ .

We are able to deduce this in the following way also. We imagine anywhere in fig. 1 on the  $P_0\pi$ -curve a point  $s$ , through which we draw a horizontal line; on this line we take a point  $s'$  in the vicinity of  $s$ . Then the point  $s$  represents an osmotic equilibrium:

$$(s) = (\text{water})_{P_0} \mid E_P \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

and the point  $s'$  an osmotic system:

$$(s') = (\text{water})_{P_0 + dP_0} \mid E_{P + dP_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

the latter arises from the first by changing the pressure on both sides of the membrane with the same amount  $dP_0$ . It now follows from (10<sup>a</sup>) and (10<sup>b</sup>):

$$\xi_0(s') = \xi_0(s) - v_0 dP_0 \quad \xi(s') = \xi(s) - \Delta V_E \cdot dP_0 \quad . \quad . \quad (41)$$

As (39) is an osmotic equilibrium,  $\xi_0(s)$  viz. the *O. W. A.* of the water is equal to  $\xi(s)$  viz. the *O. W. A.* of system  $E$ ; consequently it follows from (41):

$$\xi_0(s') - \xi(s') = (\Delta V_E - v_0) \cdot dP_0 \quad . \quad . \quad . \quad . \quad . \quad (42)$$

We now imagine the point  $s'$  in the region which is situated at the right side of the  $P_0\pi$ -curve (viz. at the right, according to the definition given above); we distinguish two cases.

a. Point  $s$  is situated on one of the branches *b e*, *e g* or *g i*, so that  $\Delta V_E < v_0$ . In order to come from  $s$  in the point  $s'$  we have to take  $dP_0$  positive, therefore. It now follows from (42):

$$\xi_0(s') < \xi(s') \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

b. Point  $s$  is situated on one of the branches *a b* or *i k*, so that  $\Delta V_E > v_0$ . In order to come from  $s$  in  $s'$  we have to take now  $dP_0$  negative; hence follows again (43).

As, therefore, (43) is valid for every point  $s'$  which is situated at the right side of the  $P_0\pi$ -curve, the rule mentioned above sub 2. follows from this.

If we take point  $s'$  at the left side of the curve, then we find, just as above:

$$\xi_0(s') > \xi(s') \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

from which follows the rule mentioned above sub 3.

(To be continued).

**Palaeontology.** — *Discoasteridae Incertae Sedis*. By TAN SIN HOK.  
(Communicated by Prof. H. A. BROUWER).

(Communicated at the meeting of February 26, 1927)

In this communication the stellate bodies of aragonite, mentioned only incidentally in the present author's article on the coccolith-limestone of Bebalain, will be discussed more fully.

First the author wants to express thanks to all those, who have directly or indirectly cooperated to find the identification of these problematic forms. Successively preparations of these *Discoasters* have been sent to Prof. S. SQUINABOL in Torino, Dr. A. FORTI in Naples, Prof. L. CAYEUX in Paris, Prof. Dr. J. SCHILLER in Vienna, and Prof. Dr. H. LOHMANN, in Hamburg, whose kindliness has put the present author under great obligations.

The forms are not novel to science. EHRENBERG mentioned them already in his „Mikrogeologie“ in 1854 <sup>1)</sup>, found in marls and limestones, originating from Placca di Furni, Zante, from Aegina, from the catacombs of Thebes, from the Anti-Libanon, from Sicily, from Caltanisetta, from Timor, from Carthago, from Barbados, from Kuh-Daëna and Dalaki in South-Persia.

He gave them the general name „Crystalldrusen“, „Scheibensternchen“ or „Crystalloids“. As appears also from these names, his opinion was that their origin was inorganic. Besides, he found asterisks <sup>2)</sup>, called *Actiniscus*, attributed to the „*Polygastern*“. These asterisks are probably *Dyctiochs* (*Silicoflagellates*), partly also spicules of sponges and are to be distinguished from the „Crystalldrusen“, on account that they are composed of silice. Originally the lime-asterisks too were called *Actiniscus* (1843), but in later works they were referred to „Unorganisches“.

Among the „Crystalldrusen“ were reckoned stellate as well as rosette-shaped „crystalloids“.

SORBY found rosette-shaped „Crystalldrusen“ in the English Chalk. According to him they are decidedly of inorganic origin <sup>3)</sup>.

In Barbados HILL found „Crystalloids“ in the calciferous oceanic deposits

<sup>1)</sup> EHRENBERG. Mikrogeologie. Pl. XXIV—66, 67; Pl. XXV B.—12, 13, 14, 15; Pl. XXVI—54a, b, c, d.; XXXVI B.—69, 70; p. 115, 156 e. o.

<sup>2)</sup> Ibid. Pl. XIX—46, 47; Pl. XX—47.

<sup>3)</sup> SORBY. Crystalloids of the Chalk, p. 197.

lying under the famous radiolarian rocks, besides in the marls, lying directly under the raised coral-reefs<sup>1)</sup>.

HAUPT described them from a marl found in the neighbourhood of Finschhafen in former German New-Guinea<sup>2)</sup>.

JUKES-BROWNE and HARRISON mention them from the west coast of Java (op. cit. p. 215).

The CHALLENGER found them in the globigerina-ooze of station 338 in the Atlantic<sup>3)</sup>, however, they are not mentioned in the text.

According to JUKES-BROWNE and HARRISON the asterisks have been found in every depth from 600—2000 fathoms. (op. cit. p. 201).

In the specimens described by HILL and HAUPT these asterisks form with the coccoliths an essential part of the rock.

Granted that the rock-fragment used for the count, gives a general notion of the whole, in the rock of Bebalain (168\*) they occur in a number of  $55 \times 10^{14}$  a cubic meter.

In the marl-specimens from other islands of the Moluccas too, they were met with in great number.

In the marine sediments collected by the Siboga-Expedition, they are not mentioned.

Notwithstanding the general distribution, geographically as well as numerically, these *Discoasters* have not drawn attention and have remained as good as unknown.

#### *On the name Discoaster.*

In literature these asterisks have not got a special name. EHRENBERG called them "Crystalldruse, Crystalloids, Scheibensternchen", JUKES-BROWNE and HARRISON called them "stellate bodies, crystalloids".

According to ZITTEL<sup>4)</sup>, EHRENBERG's "Crystalldruse" might be spicules of *Holothurians*.

However, the *Discoasters* could not be identified, either with spicules of the *Holothurians* collected by the Siboga-Expedition<sup>5)</sup>, or with the fossil rests, described by SCHLUMBERGER<sup>6)</sup>.

Among the spicules of the *Holothurians*, there are also regular forms, however, their appearance is quite different: they are small perforated plates, anchors, wheels, etc. Besides, generally their dimensions are more important, the *Discoasters* not exceeding  $35\mu$ , those of Barbados even not exceeding  $15\mu$ .

In the many rock-specimens of the Moluccas containing *Discoasters*,

1) JUKES-BROWNE & HARRISON. Barbados II. p. 177 & 216.

2) HAUPT. Ein Kreide-ähnlicher Mergel, u. s. w.

3) MURRAY & RENARD. Deepsea-Deposits, Pl. XI—4).

4) ZITTEL. Handbuch der Palaeontologie p. 560.

5) SLUITER. Holothurien der Siboga-Expedition.

6) SCHLUMBERGER. Holothuridées du Calcaire Grossier.



spicules, which might with certainty be attributed to Holothurians, have not been found, what would be inexplicable, if the *Discoasters* belonged to the Holothuroids.

In my opinion, therefore, HAECKEL's identification might be dropped and the introduction of a new name has been satisfactorily accounted for.

In the spongiology names with the suffix-"aster" are usual for certain *microscleres*: sterraster, disco-hexaster, etc., but as far as I know, not in a composition "*disco-aster*", where the number of arms is left out of consideration, so that the name proposed in the previous communication<sup>1)</sup> may be kept without any risk of confusion.

#### *Structure and mineralogical composition of the Discoaster.*

The *Discoasters* are soluble in acids; the highest value of the index of refraction is about 1.69 (Method SCHROEDER VAN DER KOLK).

The birefracton varies dependent of the position towards the axis of the microscope. The highest value occurs in a position, where the plane of the *Discoaster* is placed parallelly with the axis of the microscope (white of higher order appears as interference-colour). In a position perpendicular on this, the *Discoasters* are almost isotropic. In an intermediate position every value between these two extremes occurs.

The colouring with MOHR's salt is positive<sup>\*</sup> for aragonite.

From the homogeneous extinction appears that the *Discoaster* consists of one homogeneous aragonite crystal. In the stellate *Discoasters* one of the directions of extinction always lies according to an arm. The arm, (in forms of an odd number of radians) or the arms (in forms with an even number of radians), lying in this direction, may be called the main arm(s).

In profile the *Discoasters* extinct parallelly.

From the values of elasticity of aragonite follows that the crystallographic *c*-axis is placed perpendicularly on the plane of the *Discoaster*, the *b*- and *a*-axis being placed in that plane and probably in this way, that *b* is in the direction of the main arm. (This observation could be only executed with little accuracy, as  $b = \gamma = 1,686$ ; and  $a = \beta = 1,682$  and  $\gamma - \beta = 0,004$  is, given the minute thickness of the *Discoaster*, too small to be able to fix the positive or negative character with accuracy. The fact mentioned by HILL that in the same preparation the *Discoaster* shows two extremes of double refraction has its origin in the fact, that they are lying in different position towards the axis of the microscope.

If a *Discoaster* is rotated round an axis in the plane of the arms, then the interference-colours are seen to pass from one extreme to the other.

#### *The organic origin of the Discoaster.*

According to EHRENBURG and SORBY, as mentioned above, these proble-

<sup>1)</sup> TAN SIN HOK. Young-Tertiary Limestone of Rotti.

matica have nothing to do with organisms. SORBY's opinion (op. cit. p. 197) was that they are nothing but crystals, radially arranged round a fragment of a foraminiferal shell as a nucleus.

The hexaradiati often occurring in the Moluccas should make one suppose that they are nothing but sixfold twins of aragonite, consequently belonging to mineralogy.

From the behaviour between crossed nicols appears quite clearly, that we have to do with one homogeneous crystal. Further, the varying number of arms, the form of the separate arms, the convexo-concavely curved plane of the *Discoaster* gives conclusively proof of an organic origin.

An inorganic origin consequently may be considered out of question. That the *Discoaster* is constructed of aragonite is nothing peculiar, aragonite regularly occurs as building-stone of skeletons.

### *System of the Discoaster.*

Fam. *Discoasteridae* incert. sed. nov. fam.

*Actiniscus septenarius* Ehrenberg. 1843. Monatsber. Ak. Wiss. Berl.

The rosette-shaped as well as the stellate bodies are considered as belonging to this family. They have in common their mineralogical composition of aragonite, the orientation of the axes of elasticity in the disks. By transitions the *Helio-discoasters* are connected with the *Eu-discoasters*, the *Eu-discoasters* with the *Hemidiscoasters*, so that it is motivated to attribute the rosette-shaped disks with the asterisks to the *Discoasteridae*.

As far as known, their diameter does not exceed  $35\mu$ . Three groups can be distinguished, which are looked upon as genera.

#### 1. Genus: *Helio-discoaster* nov. gen.

To this are attributed all rosette-shaped *Discoasters*. The arms (sectors) are not separated: they fill the disk entirely. In the center a nucleus may be present.

In preparations of the Moluccas the *Helio-discoasters* are not frequent. In Barbados they occur in great numbers, the forms with nucleus being regular. These nuclei are thought to be caused, because in the center, where the arms meet, they are drawn into the direction of the disk axis <sup>1)</sup>.

Forms in which this structure could be examined, have not been found in the Moluccas. The nuclei are small here, they are to be considered as rests of the nuclei of the *Helio-Discoaster* of Barbados, in many cases they are entirely absent.

The disk of the *Helio-discoaster* is flat, not curved convex-concavely as in the next two groups.

Distinguished are:

<sup>1)</sup> JUKES-BROWNE & HARRISON. Loc. cit. p. 178 fig. 4, 5 en 6.

*Discoaster Barbadiensis* nov. spec. typ.

EHRENBERG, Mikrogeologie 1854. Pl. XXIV — 67, and A.; Pl. XXV — 13, 14, 15, p. 155.

SORBY, Crystalloids of the Chalk, Ann. Mag. Nat. Hist. Vol. VIII, 1861, p. 197.

JUKES-BROWNE & HARRISON, Barbados II, Quart. Journ. Geol. Soc., London. Vol. XLVIII, 1892, p. 178, fig. 4, 5 and 6.

With 11—21 arms (sectors) filling the disk entirely. In the center the arms are drawn axially by which a nucleus originates. Size generally  $15\ \mu$  and less.

*Discoaster Barbadiensis* var. *Bebalaini*, fig. 4.

Differs from the previous in the strongly reduced nucleus. As only a few specimen could be examined, it could not be traced, if *D. Barbadiensis* typ. was present. The variety *Bebalaini* is a transition to the

*Discoaster Ehrenbergi* nov. spec.

With 11—21 arms without nucleus. Named after the discoverer of these problematical bodies.

2. Genus: *Eu-Discoaster* nov. gen.

To this genus belong all stellate *Discoasters*, the arms of which can be distinguished from each other until the center of the disk.

They can be derived from the *Helio-Discoasters* without the least difficulty (comp. figs. 2, 3, 5, 6, etc.)

The number of arms varies from 5—8. The species are distinguished by the number of arms. The plane of the *Discoaster* is curved convexo-concavely, fig. 8a. With some a nucleus could be found in the center, analogical with that of *D. Barbadiensis*.

*Discoaster Hilli* nov. spec.

JUKES-BROWNE & HARRISON, Barbados II, p. 178, fig. 3.

With 8 cylindrical arms, subordinate in *Bebalain*; a form which often occurs in Barbados.

*Discoaster Brouweri* nov. spec. typ, Figs. 8a, 8b.

With 6 cylindrical arms, predominant in the Moluccas. Figs. 8b is the *D. Brouweri* in profile.

*D. Brouweri* var.  $\alpha$  Fig. 13.

The arms are thickened distally, not ramified.

*D. Brouweri* var.  $\beta$  Fig. 6.

The arms are distally not thickened, provided with a notch.

*D. Brouweri* var.  $\gamma$  Fig. 7.

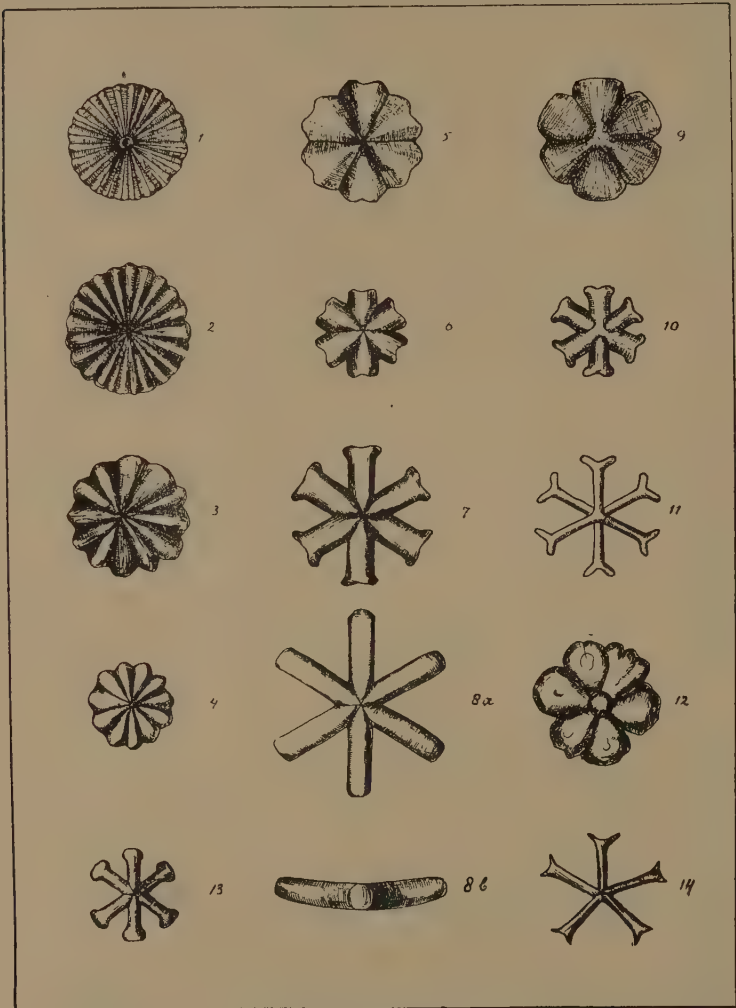
The arms are thickened distally and ramified.

*D. Brouweri* var.  $\delta$  Fig. 5.

The arms are petaloid. Not frequent.

*Discoaster pentaradiatus* nov. spec. var.  $\gamma$  Fig. 14.

5 arms. The same varieties can be distinguished as mentioned above.



Enlargement:  $2000 \times$  <sup>1)</sup>.

3. Genus; *Hemi-Discoaster* nov. gen.

Hereby those *Discoasters* are meant, where groups of arms have grown together without joints. In the preparations of the Moluccas only the hexa- and tri-radiati of this group have been found. Here the arms which form an interval of  $120^\circ$ , have grown two and two together.

<sup>1)</sup> As to the explanation, see page 419.

In connection with the joining of the arms the *Hemi-Discoasters* have less possibilities of variety in the number of arms. As to the varieties of the shape of the radii, they form a parallel series with the *Eu-Discoasters*.

They can be derived from the *Eu-Discoasters* (Fig. 10). The plane in which the arms are situated is curved convex-concavely.

*Discoaster Molengraaffi* nov. spec. typ.

MURRAY & RENARD, Deep-sea Deposits, Pl. XI — 4.

The arms have the same form as the *D. Brouweri* typ. The same varieties as mentioned above can be distinguished.

*D. Molengraaffi* and *D. Brouweri* are the predominant forms in the Moluccas. Of both species the variety  $\delta$  is least frequent.

*D. triradiatus* nov. spec. typ.

With 3 cylindrical arms;  $\alpha$ - and  $\beta$ -varieties are found. This species occurs sporadically.

Remark: The *Hemi-Discoasters* are easily to be derived from the *Eu-Discoasters* by the growing together of the 1<sup>st</sup>, 3<sup>d</sup> and 5<sup>th</sup> arm. Transitions from the *Eu*- to the *Hemi*-joining are found, fig. 10.

As to the forms of the arms the *Discoasters* of the two genera form parallel series.

*Comparison with the Discoasteridae of Barbados.*

In Barbados the *Helio-Discoasters* are frequent, the forms with a nucleus are regular. Among the stellate *Discoasters* the 8-radiati are predominant, forms with a nucleus are not met with, the other species are less common. The *Discoasters* of Barbados are smaller on the whole, the largest is 15  $\mu$ .

In the Moluccas the stellate *Discoasters* are the predominant forms, generally they have the same size as those of Barbados; the hexa-radiati occur most frequently; forms with a nucleus are found, 8-radiati are subordinate. *Helio-Discoasters* are rare.

Remarkable is that relations are as good as complimentary.

*Discoasteridae and Coccolithophoridae.*

From the figures, appears that in some cases in outward appearance, a striking resemblance with the coccoliths may be found. *D. Ehrenbergi* (fig. 2) resembles strikingly a placolith (fig. 1), however, the axis-channel is missing and, besides, the structure of a coccolith is radially-fibred, so that in the latter, between crossed nicols an interference-cross becomes visible.

The *D. Molengraaffi* var.  $\delta$  shows much resemblance to the "coccolith" figured by SCHMIDT<sup>1)</sup>, found in the (...) sediments of Brindisi, which,

<sup>1)</sup> SCHMIDT, Coccolithen und Rhabdolithen, p. 675, Pl. I, fig. 10.



however, Prof. LOHMANN, is not willing to reckon among the *Coccolithophoridae*. (Private communication).

However great the resemblance, Prof. LOHMANN and Prof. SCHILLER think any relation to the *Coccolithophoridae* excluded.

*The way of living of the Discoasteridae.*

They are certainly marine organisms, until now the skeletons have only been found in marine deposits. From the small size of the *Discoasters* and the convexo-concave curving of the plane in which the arms are situated, some supposition may be derived, regarding size and form of these organisms.

They must have been microscopically small and may have a spherical form. Possibly, analogical with the coccoliths, the *Discoasters* act as covering of the cell.

The finding of these *Discoasters* exclusively in oceanic sediments or in sediments with oceanic character may be connected with a planctonic mode of living.

*Geological age of the Discoasters.*

Besides the finding of the *D. Barbadiensis* by SORBY in English Chalk, the stellate *Discoasters* have only been found in Young-Tertiary and Quaternary deposits, as far as the age of the deposits mentioned is known to me. Their composition of labile aragonite, their delicate forms make the finding in older sediments improbable.

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13. ZITTEL, K. A. VON, Handbuch der Palaeontologie. Bd. I, 1876—80, p. 560.

EXPLANATION: (Enlargement 2000  $\times$ ).

- Fig. 1. Placolith (*Coccolithophora leptophora* MURR. & BLACKM.)  
 " 2. Discoaster Ehrenbergi nov. spec.  
 " 3. " Ehrenbergi nov. spec.  
 " 4. " Barbadiensis nov. spec., var. Bebalaini.  
 " 5. " Brouweri nov. spec., var.  $\delta$  transition from the Helio- to the Eu-discoaster.  
 " 6. " Brouweri nov. spec., var.  $\beta$ .  
 " 7. " Brouweri nov. spec. var.  $\gamma$ .  
 " 8a. " Brouweri nov. spec. typ.  
 " 8b. " Brouweri nov. spec. typ. in profile.  
 " 9. " Molengraaffi nov. spec., var.  $\delta$ .  
 " 10. " Molengraaffi nov. spec. var.  $\gamma$ , transition from Eu- to Hemi-discoaster.  
 " 11. " Molengraaffi nov. spec., var.  $\gamma$ .  
 " 12. " "Coccolith" from Brindisi, SCHMIDT. op. cit. Pl. I, fig. 10.  
 " 13. " Brouweri nov. spec., var.  $\alpha$ .  
 " 14. " pentaradiatus nov. spec., var.  $\gamma$ .

*Delft, Laboratory for Historical Geology and Palaeontology.*

February 1927.

**Physiology.** — *On some Properties of the Radiation-substances (with weak radiation).* By Prof. H. ZWAARDEMAKER.

(Communicated at the meeting of March 26, 1927).

In the November meeting of the Koninklijke Akademie van Wetenschappen the present writer demonstrated that radio-active radiation (radium rays of weak penetrating power, polonium rays) generates in the heart-muscle peculiar substances, which restore contractions of the heart that have ceased through deprivation of potassium <sup>1</sup>). Such an experiment succeeds best, when the organ is connected up in a small circulation of only 30 c.c. of liquid. This liquid (Ringer's potassium free solution) can be kept running by introducing air into a vertical portion of the course, along a small tube placed in a line with the direction of the stream. The air-bubbles carry the liquid upwards until it reaches the glass sphere open at the top, and can descend to the heart (eel-heart on glass canula in sinus or frog-heart on Kronecker canula. From the heart this liquid passes to an open receptacle, from which the liquid is again pumped up etc. <sup>2</sup>).

When such a heart has first come to a standstill through Ringer's solution without potassium (occasionally automatic), i. e. without washing out  $\frac{1}{3}$  of the potassium, we proceed to radiation from three sides, e. g. with radiofères of enamel  $1.6 + 1.8 + 1.9$  or plates covered with polonium of one square cm. <sup>3</sup>). After a latent period of from  $\frac{1}{2}$  to 1 hour the heart begins to beat. Gradually the radiation substances in question, of which we are going to describe the properties, will then appear in the liquid.

In a second circulation such a liquid can also set another heart beating that has beforehand been treated in the same way, thanks to the presence of the radiation substance. The experiment may, however, also be carried out without resorting to a renewed circulation of the old liquid, by connecting a second heart, prepared in the same manner, in series with the first organ in the old circulation. Then the same liquid first perfuses the radiated heart, and subsequently a non-radiated one. The result is that after the radiated heart has begun to pulsate, the second non-radiated organ will also begin. The two hearts can be made to record the curve on one and the same smoked surface.

<sup>1</sup>) H. ZWAARDEMAKER, Kon. Akad. v. Wet., Amsterdam, 27 Nov. 1926.

<sup>2</sup>) NOYONS et BELEHRADEK, C. R. Soc. de biol. T. 88, p. 621, 1920.

<sup>3</sup>) H. ZWAARDEMAKER, Pflüger's Archiv Bd. 213, p. 757, 1926; *ibid.* Bd. 215, p. 460, 1927.

Such a graph is represented in our figure. The bottom curve registers the pulsation of the radiated heart (enamel radiofères), the top one that of the non-radiated organ. Initially the rhythm of the former heart, which commenced earlier, is quicker than that of the latter, but this changes as the experiment advances and the pulsations, not evoked by direct radiation, become better. Thus things go on for hours. All the while, besides radiation-substances some potassium-ions, also appear in the circulating fluid. These ions issue from the so-called fixed potassium of the muscles. Obviously their quantity is only small, so that they cannot of themselves evoke pulsations<sup>1)</sup>. The latent period is of interest. It is essential to the effect of the radiation, but also to that of the radiation-substance. It stands to reason that when the hearts are equally sensitive, the effect of the radiation substance follows that of the radiation, since

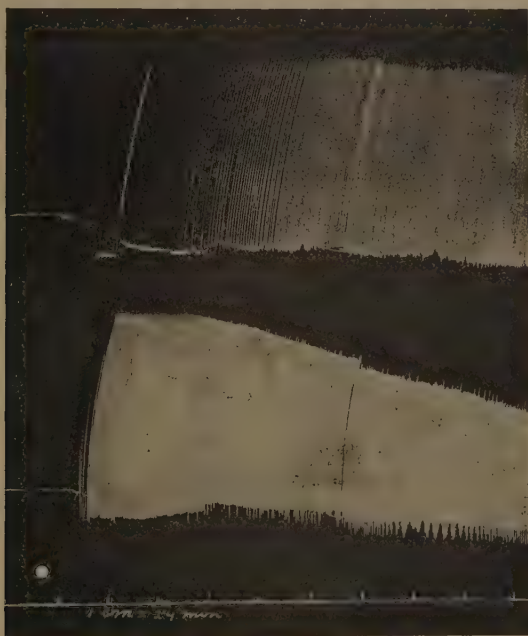


Fig. 1.

2 eel-hearts in one and the same circulation of 30 cc. of liquid.

*Bottom-curve*; the organ under direct radiation.

*Top-curve*: the organ under indirect radiation. At the site of the speck radiation was started. (1 scale mark of the time-line represents 24 min.).

<sup>1)</sup> These potassium-ions can emanate only from the muscles. Measured by the standard of the frog-tissue the two hearts contain 2 pro mille, or in 200 mgrs of muscle 0.4 mg K. Of this quantity only 0.12 mg can pass into the fluid.

this substance appears first in the heart subjected to direct radiation, subsequently in the liquid and finally in the second heart.

It is no trouble next morning to examine in every direction the liquid, which has been kept in circulation a whole night with the results illustrated above for both hearts.

Thanks to the valuable aid of Mr. Ph. ARONS, we were able in a few months to observe the properties of a large number of similar perfusion fluids. It appeared that the radiation-substance present in these fluids is

dialysable,  
ultrafilterable,  
thermostable,  
adsorbable to carbon and magnesium-silicate,  
soluble in alcohol.

This is the case with the radiation-substance originating under the influence of polonium-radiation, as well as with the substance coming forth under the influence of radium-radiation.

Moreover the said radio-substances do not appreciably lower the surface-tension of water (dynamic measurement)<sup>1)</sup>. Neither do they yield an adsorption-band in the ultraviolet, which other similar substances do.

With intenser and quicker radiation other radiation-substances will presumably develop, whose effect we suspected in the radiated heart.

Consequently this heart very often does not beat so well as the heart subjected to indirect radiation.

The long latency (48 minutes for direct radiation, 20 minutes after the addition of the radiation-substance in the perfusion-fluid) renders it probable that we have to do here with substances acting catalytically. They are probably identical with the „substances actives” previously described by J. DEMOOR<sup>2)</sup>, resp. the heart hormones of L. HABERLANDT<sup>3)</sup> in normal life. As we have to differentiate two independent radiation-substances, the one produced by the  $\alpha$ -rays, and the other by the  $\beta$ -rays, the catalytic substances, concerned here, have in this paper always been spoken of in the plural.

<sup>1)</sup> R. BRINKMAN, Abderhalden's Hdb. d. Biol. Arbeitsmethoden, Abt. IV, Teil 4, Heft 6, 1927.

<sup>2)</sup> J. DEMOOR, Arch. int. de Physiol. t. 20, p. 29, 446, 1922; t. 23, p. 121, 1924; Bruxelles méd. 13 Sept. 1925.

<sup>3)</sup> L. HABERLANDT, Klin. Wochenschr. 1924, N<sup>o</sup>. 36, Das Hormon der Herzbewegung, Berlin—Wien 1927.



**Mathematics.** — *The Definition of Euclidean Measure in the Projective Plane.* By O. BOTTEMA. (Communicated by Prof. W. VAN DER WOUDE).

(Communicated at the meeting of March 26, 1927).

Euclidean metrics in the plane are fixed by choosing 2 conjugate complex points  $I_1$  and  $I_2$ , the isotropic points.

The projective transformations that leave these points invariant, form the group of similitude. The definition of *angular measure* rests immediately on the projective invariant par excellence, the *anharmonic ratio*. For, if  $A$ ,  $B$  and  $C$  are three points of the plane, according to the formula of LAGUERRE:

$$\angle BAC = \frac{1}{2i} \log A(I_1 I_2 BC),$$

where  $A(I_1 I_2 BC)$  is the anharmonic ratio of the rays  $AI_1$ ,  $AI_2$ ,  $AB$  and  $AC$ .

The definition of *distance* is less simple. It is often given as the limit of the expression which holds good in non-euclidean geometry, where angle and distance are entirely dualistic and the latter is likewise defined by the aid of an anharmonic ratio.

In what follows we shall give a direct definition of distance that is entirely based on anharmonic ratios.

We must notice that by choosing  $I_1$  and  $I_2$  only *ratios* of distances will be defined. For the definition of ratios of distances it is further sufficient to restrict ourselves to the comparison of segments that have a common extremity as after introducing the straight line at infinity, we can already ascertain the equality of parallel line segments.

If  $\overline{AB}$  and  $\overline{AC}$  represent the lengths of the segments we give the following definition:

$$\overline{AB}^2 : \overline{AC}^2 = I_1(I_2 ABC) \cdot I_2(I_1 ABC).$$

The square of the ratio of the distances is the product of two anharmonic ratios.

In order to prove that this definition agrees with the usual definition of length we choose the homogeneous coordinates of  $I_1$  and  $I_2$  resp.  $(1, i, 0)$  and  $(1, -i, 0)$ , and the Cartesian coordinates of  $A$ ,  $B$  and  $C$  resp.  $(a_1, a_2)$ ,  $(b_1, b_2)$ ,  $(c_1, c_2)$ . The four lines  $I_1 I_2$ ,  $I_1 A$ ,  $I_1 B$ ,  $I_1 C$  cut the  $Y$ -axis at four points of which the  $Y$ -coordinates are resp.:

$$\infty, (a_2 - ia_1), (b_2 - ib_1), (c_2 - ic_1),$$

so that

$$I_1(I_2 ABC) = \frac{(b_2 - ib_1) - (a_2 - ia_1)}{(c_2 - ic_1) - (a_2 - ia_1)} = \frac{(b_2 - a_2) - i(b_1 - a_1)}{(c_2 - a_2) - i(c_1 - a_1)},$$

and for  $I_2(I_1 ABC)$  the conjugate complex value is found.

We find, therefore, in fact:

$$I_1(I_2 ABC) \cdot I_2(I_1 ABC) = \frac{(b_1 - a_1)^2 + (b_2 - a_2)^2}{(c_1 - a_1)^2 + (c_2 - a_2)^2} = \frac{\overline{AB}^2}{AC^2}.$$

The sides and the angles of a triangle  $ABC$  are now defined in a similar way, viz. as functions of the anharmonic ratios of the four rays drawn out of each of the five points  $I_1, I_2, A, B, C$  to each of the other four. These anharmonic ratios are the most simple projective invariants of the quintuple. They are for the rest equal to the anharmonic ratios of any four of the points of the conic which can be passed through the quintuple, which, speaking metrically, is the circumscribed circle about the triangle  $A, B, C$ . Not every function of the anharmonic ratios is an invariant of the triangle; it is necessary that  $I_1$  and  $I_2$  appear symmetrically.

The definitions of angle and distance agree still more if we write the anharmonic ratio that appears in the angular measure, likewise as the product of two anharmonic ratios. So e.g.:

$$A(I_1 I_2 BC) = B(I_2 I_1 CA) \cdot C(I_2 I_1 AB).$$

The given definitions may be used to prove simple theorems of Euclidean geometry by the aid of projectivity.

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**Mathematics.** — *Ueber das Verhältniß separabler Räume zu kompakten Räumen* <sup>1)</sup>. By Dr. W. HUREWICZ. (Communicated by Prof. L. E. J. BROUWER).

(Communicated at the meeting of March 26, 1927).

Sei  $R$  ein separabler metrisierbarer topologischer Raum, ein Raum also, der laut einem Theorem von URYSOHN <sup>2)</sup> als Teilmenge eines kompakten metrisierbaren Raumes betrachtet werden kann. Es entsteht die Frage, ob es unter den  $R$  enthaltenden kompakten metrisierbaren Räumen stets auch solche gibt, deren Dimension mit der Dimension von  $R$  übereinstimmt. Wir wollen zeigen, dass dies tatsächlich der Fall ist. Es gilt m. a. W.:

**Theorem.** *Jeder separable metrische Raum  $R$  ist homöomorph mit einer Teilmenge eines kompakten metrischen Raumes, welcher dieselbe Dimension besitzt wie  $R$ .* <sup>3)</sup>

Den Beweis stützen wir auf die folgende Verallgemeinerung eines bekannten dimensionstheoretischen Satzes von Menger und URYSOHN <sup>4)</sup>:

I. Ist  $R$  ein separabler <sup>5)</sup> Raum von der endlichen Dimension  $n$ , und  $\mathcal{S}$  ein endliches System offener Mengen  $G_1, G_2, \dots, G_p$ , deren Summe  $R$  ist, so gibt es ein System abgeschlossener Mengen  $F_1, F_2, \dots, F_q$  mit den folgenden Eigenschaften:

1. Jeder Punkt von  $R$  liegt in mindestens einer und in höchstens  $n+1$  Mengen  $F_i$ ;

2. Jedes  $F_i$  ist einer Menge  $G_k$  enthalten. <sup>6)</sup>

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<sup>1)</sup> Eine ausführliche Darstellung wird in den Math. Am. erscheinen.

<sup>2)</sup> Vgl. Math. Ann. 92, S. 303.

<sup>3)</sup> In diesem Theorem ist auch das Ergebnis von TUMARKIN (vgl. diese Proceedings 28, S. 996) enthalten, wonach jeder separable metrische Raum mit einer Teilmenge eines dieselbe Dimension besitzenden vollständigen Raumes homöomorph ist.

<sup>4)</sup> Nämlich, des Satzes, dass ein kompakter  $n$ -dimensionaler Raum für jede positive Zahl  $\varepsilon$  in endlich viele abgeschlossene Mengen mit Durchmessern  $< \varepsilon$  zerlegt werden kann, die zu je  $n+2$  leere Durchschnitte haben. Vgl. Menger, Monatshefte f. Math. u. Phys. 34, S. 153. URYSOHN, Fund. Math. 8, S. 292.

<sup>5)</sup> Es werden hier, wie auch überall in Folgenden, ausschliesslich metrische bzw. metrisierbare Räume betrachtet.

<sup>6)</sup> Falls  $R$  kompakt ist, gibt es bei vorgegebenen Mengen  $G_i$ , wie leicht ersichtlich, eine Zahl  $\varepsilon > 0$ , derart, dass jede Menge mit Durchmesser  $< \varepsilon$  in einer der Mengen  $G_i$  enthalten ist. Für den Fall kompakter Räume ist daher Satz I mit dem sub <sup>4)</sup> angeführten Satz von Menger und URYSOHN äquivalent.

Zum Beweise ist es bequem Satz I. in diese Gestalt zu bringen:

*I'*. Ist die in einem separablen Raum gelegene  $n$ -dimensionale Menge  $M$  in der Summe der endlich vielen offenen Mengen  $G_1, G_2, \dots, G_p$  enthalten, so kann  $M$  mit endlich vielen offenen Mengen  $U_1, U_2, \dots, U_q$  überdeckt werden, deren jede in einem  $G_i$  enthalten ist, und die zu je  $n+2$  leere Durchschnitte haben.

Aus *I'*. folgt sofort *I.*: Man bilde nämlich zu den Mengen  $U_i$  von Satz *I'*. ein System von  $q$  in  $M$  abgeschlossenen Mengen  $F_i$ , so dass  $F_i \subset U_i$  ( $i = 1, 2, \dots, q$ ) und  $M = \sum_{i=1}^q F_i$ ,<sup>7)</sup> so befriedigen die Mengen  $F_i$  die Forderungen des Satzes *I* in Bezug auf das System der in  $M$  offenen Mengen  $G_i M$ . (Ebenso einfach kann man zeigen, dass umgekehrt aus *I.* *I'*. folgt).

Wir beweisen die Behauptung *I'*. zuerst für  $n=0$ . Zu jedem Punkt von  $M$  gibt es dann eine Umgebung, deren Begrenzung zu  $M$  fremd ist, und die in einer der  $p$  Mengen  $G_i$  enthalten ist.  $M$  wird (mit Rücksicht auf die Separabilität des Raumes) von abzählbar vielen derartigen Umgebungen  $V_1, V_2, V_3, \dots$  überdeckt. Setzen wir  $W_1 = V_1$  und  $W_m = V_m - (\bar{V}_1 + \bar{V}_2 + \dots + \bar{V}_{m-1})$  ( $m = 2, 3, \dots$ ) und bezeichnen wir mit  $U_i$  ( $i = 1, 2, \dots, p$ ) die Summe aller derjenigen  $W_m$ , die in  $G_i$ , aber in keinem  $G_k$  für  $k < i$  enthalten sind, so genügen die  $p$  offenen Mengen  $U_i$ , wie man leicht sieht, den Forderungen des Satzes *I'*, der somit für den Fall  $n=0$  bewiesen ist.

Nehmen wir jetzt an, Satz *I'* sei richtig, wenn man in ihm die Zahl  $n$  durch eine kleinere ersetzt, und zerspalten wir die gegebene  $n$ -dimensionale Menge  $M$  in einen  $(n-1)$ -dimensionalen Teil  $^{n-1}M$  und einen 0-dimensionalen Teil  $^0M$ .<sup>8)</sup> Nach Annahme lässt sich  $^{n-1}M$  (bzw.  $^0M$ ) mit endlich vielen offenen Mengen  $U_1, U_2, \dots, U_q$  (bzw.  $U'_1, U'_2, \dots, U'_r$ ) überdecken, die Teilmengen der  $G_i$  sind und zu je  $n+1$  (bzw. zu je zwei) leere Durchschnitte haben. Die  $q+r$  Mengen  $U_i$  und  $U'_i$  bilden zusammen ein System von den im Satz *I'* verlangten Eigenschaften.

Sei jetzt  $R$  separabler Raum von der endlichen Dimension  $n$ <sup>9)</sup> den wir auf eine Teilmenge eines  $n$ -dimensionalen kompakten Raumes topologisch abbilden wollen. Wir setzen voraus (auf Grund des erwähnten URYSOHN'schen Theorems),  $R$  sei bereits als Teilmenge eines kompakten Raumes (von einer unbekannten Dimension) gegeben. Dann ist bekanntlich  $R$  für jedes  $\varepsilon > 0$  Summe von endlich vielen in  $R$  offenen Mengen mit Durchmessern  $< \varepsilon$ <sup>10)</sup>.

Wir betrachten eine beliebige gegen 0 konvergierende Folge positiver Zahlen  $\varepsilon_m$  und bestimmen für jede natürliche Zahl  $m$  ein System abgeschlossener Mengen

$$\mathfrak{G}_m = \{F_1^m, F_2^m, \dots, F_{k_m}^m\}$$

gemäss den folgenden Bedingungen:

1. Es gilt  $R = \sum_{i=1}^{k_m} F_i^m$ , ( $m = 1, 2, \dots$ ) und jeder Punkt von  $R$  gehört (bei festem  $m$ ) höchstens  $n+1$  Mengen  $F_i^m$  an.

<sup>7)</sup> In jedem metrischen Raum gilt der Satz: Ist  $M$  eine beliebige Menge und  $G_1, G_2, \dots, G_p$  offene Mengen, so dass  $M \subset \sum_{i=1}^p G_i$ , so gibt es  $p$  in  $M$  abgeschlossene Mengen  $F_i$  ( $i = 1, 2, \dots, p$ ) mit den Eigenschaften:  $F_i \subset G_i$ ;  $M = \sum_{i=1}^p F_i$ .

<sup>8)</sup> Vgl. HUREWICZ, Math. Ann. **96**, S. 761, sowie TUMARKIN, a.a.O.

<sup>9)</sup> Ist  $R$   $\infty$ -dimensional, so hat jeder  $R$  enthaltende topologische Raum dieselbe Dimension wie  $R$ .

<sup>10)</sup> Vgl. HAUSDORFF, Grundzüge der Mengenlehre (Leipzig, 1914), S. 313—315.

2. Die Durchmesser aller  $F_i^m$  sind  $< \varepsilon_m$ .

3. Ist (für  $m \geq 2$ )  $\mathfrak{S}'_{m-1}$  das Vereinigungssystem der Systeme  $\mathfrak{S}_1, \mathfrak{S}_2, \dots, \mathfrak{S}_{m-1}$  (d. h. das System aller Mengen, die einem der Systeme  $\mathfrak{S}_i$  ( $i < m$ ) angehören), und sind  $A_1, A_2, \dots, A_r$  irgend welche Mengen aus  $\mathfrak{S}'_{m-1}$ , die keinen gemeinsamen Punkt besitzen, so hat keine Menge des Systems  $\mathfrak{S}_m$  mit sämtlichen  $A_i$  Punkte gemein.

Dass man die Systeme  $\mathfrak{S}_m$  in Einklang mit diesen Bedingungen wirklich bestimmen kann, ist eine Folgerung aus Satz I. Sei nämlich  $m$  eine natürliche Zahl; denken wir uns die Systeme  $\mathfrak{S}_1, \mathfrak{S}_2, \dots, \mathfrak{S}_{m-1}$  und folglich aus das System  $\mathfrak{S}'_{m-1}$  bereits definiert, und bezeichnen wir für jeden Punkt  $p$  von  $R$  mit  $A_{m-1}(p)$  die Summe aller Mengen des Systems  $\mathfrak{S}'_{m-1}$ , die  $p$  nicht enthalten. (Die Mengen  $A_{m-1}(p)$  bilden natürlich ein *endliches* System). Sodann zerlegen wir  $R$  in endlich viele offene Mengen  $U_1^m, U_2^m, \dots, U_{k_m}^m$  mit Durchmessern  $< \varepsilon_m$  und bestimmen auf Grund von 1. die Mengen  $F_i^m$  in der Weise, dass die Bedingung 1 besteht und dass jedes  $F_i^m$  in einer der endlich vielen offenen Mengen  $U_k^m(R - A_{m-1}(p))$  (die in ihrer Gesamtheit  $R$  überdecken), enthalten sei. Dann sind, wie man sofort bestätigt, auch die Bedingungen 2 und 3 erfüllt.

Setzen wir der Einfachheit halber  $F_i^m = 0$  für  $i > k_m$ , und bezeichnen wir für jedes System  $\alpha$  aus endlich vielen verschiedenen natürlichen Zahlen  $m_1, m_2, \dots, m_r$  mit  $F_\alpha^i$  den Durchschnitt  $F_{m_1}^i \cdot F_{m_2}^i \cdot \dots \cdot F_{m_r}^i$ . Eine unendliche Folge:

$$\alpha_1, \alpha_2, \alpha_3, \dots$$

von Systemen natürlicher Zahlen nennen wir eine *Kette*<sup>11)</sup>, wenn folgendes gilt:

(a) Für jedes  $m$  ist

$$\prod_{i=1}^m F_{\alpha_i}^i \neq 0;$$

(b) Die Folge  $\{\alpha_i\}$  verliert die Eigenschaft (a), sobald irgend eines ihrer Glieder  $\alpha_i$  durch ein System natürlicher Zahlen  $\alpha'_i$  ersetzt wird, in dem  $\alpha_i$  als echtes Teilsystem enthalten ist. Es gilt m.a.W. für jede nat. Zahl  $p$ , die kein Element ist von  $\alpha_i$ :

$$(x) \quad F_p^i \cdot \prod_{j=1}^m F_{\alpha_j}^j = 0$$

für mindestens einen Index  $m$ .

Aus 3. ergibt sich leicht:

(') Sind  $\{\alpha_i\}$  und  $\{\beta_i\}$  zwei *verschiedene* Ketten, (d. h. ist für mindestens einen Index  $i$   $\alpha_i$  von  $\beta_i$  verschieden), so sind die Systeme  $\alpha_i$  und  $\beta_i$  für *alle hinreichend grosse*  $i$  elementenfremd.

In der Tat sei  $p$  eine natürliche Zahl, die in  $\beta_i$ , aber nicht in  $\alpha_i$  vorkommt. Dann ist die Gleichung (x) für einen Index  $m$  erfüllt. Ist nun  $m'$  grösser als die beiden Zahlen  $i$  und  $m$ , so gibt es nach 3) keine Menge  $F_{p'}^{m'}$ , die mit den beiden Mengen

$$(0) \quad F_p^i \cdot \prod_{j=1}^m F_{\alpha_j}^j$$

<sup>11)</sup> Vgl. ALEXANDROFF, Math. Ann. 96, S. 489. Die folgenden Ueberlegungen lehnen sich eng an den Gedankengang dieser ALEXANDROFF'schen Abhandlung an.



Punkte gemein hat. Ist aber  $q$  ein Element von  $\beta_{m'}$  (bzw. von  $\alpha_{m'}$ ), so hat  $F_q^{m'}$ , per Definitionseigenschaft (a) der Ketten zufolge, mit der ersten (bzw. mit der zweiten) der Mengen  $(^0)$  Punkte gemein. Folglich haben die Systeme  $\alpha_{m'}$  und  $\beta_{m'}$  keine gemeinsame Elemente.

Sei jetzt  $\{a_i\}$  eine beliebige Kette,  $m$  eine natürliche Zahl. Die Gesamtheit aller Ketten  $\{\beta_i\}$ , für die  $\beta_1, \beta_2, \dots, \beta_m$  Untersysteme sind von  $a_1$ , bzw.  $a_2, \dots$ , bzw.  $\alpha_m$ , nennen wir die  $m$ -te Umgebung der Kette  $\{a_i\}$ . Durch diese Festsetzung wird, wie sich auf Grund von  $(^1)$  bei Berufung auf einen Satz von ALEXANDROFF ergibt <sup>12)</sup>, ein kompakter metrisierbarer topologischer  $R^*$  von der Dimension  $n$  definiert, dessen Elementevorrat aus sämtlichen Ketten besteht.

Wir wollen jetzt eine topologische Abbildung zwischen  $R$  und einem Teil des soeben definierten Raumes  $R^*$  herstellen. Zu diesem Zwecke betrachten wir einen Punkt  $x$  von  $R$  und bezeichnen für jedes  $m$  mit  $\alpha_m(x)$  das System aller natürlicher Zahlen  $n_i$  für die der Punkt  $x$  in  $F_{n_i}$  enthalten ist. Die Folge  $\{a_i(x)\}$  ist, wie man leicht einsieht, eine Kette.

Die Bedingung (a) ist nämlich in trivialer Weise erfüllt. Die Bedingung (b) folgt daraus, dass die Mengen  $F_{\alpha_m}^m$  (wo  $\alpha_m = \alpha_m(x)$  gesetzt ist) mit wachsendem  $m$  nach 1) unendlich klein werden und sich daher auf den Punkt  $x$  zusammenziehen. Ist also die Zahl  $p$  kein Element von  $\alpha_i$ , d.h. liegt  $x$  in der offenen Menge  $R - F_p^i$ , so gilt bei hinreichend grossem  $m: F_{\alpha_m}^m \subset R - F_p^i$ , somit  $F_{\alpha_m}^m \cdot F_p^i = 0$ .

Jedem Punkt von  $R$  ist also eine Kette zugeordnet. D.h. es liegt eine Abbildung des Raumes  $R$  auf einen Teil des höchstens  $n$ -dimensionalen kompakten Raumes  $R^*$  vor, und man zeigt leicht, dass diese Abbildung umkehrbar eindeutig und beiderseits stetig ist <sup>13)</sup>. Damit ist der Beweis unseres Theorems erbracht.

Aus dem Bewiesenen ergeben sich vor allem wichtige Folgerungen hinsichtlich der MENGER'schen grundlegenden Untersuchungen über das

<sup>12)</sup> Vgl. ALEXANDROFF, a.a.O. Um an die ALEXANDROFF'sche Terminologie anzuknüpfen, müssen wir ein System  $\alpha$  natürlicher Zahlen mit der Eigenschaft  $F_\alpha^m \neq 0$  als einen Simplex des  $m$ -ten Komplexes bezeichnen (Für jedes  $m$  besteht der  $m$ -te Komplex aus einer nur endlichen Anzahl von Simplexes) und unter einer Gruppe eine endliche Folge

$$[\alpha_1, \alpha_2 \dots \alpha_m]$$

verstehen, wo  $\alpha_i$  ein Simplex des  $i$ -ten Komplexes ist ( $i = 1, 2, \dots, m$ ), und  $\prod_{i=1}^m F_{\alpha_i}^i \neq 0$  gilt. (Eine Kette ist demnach in Uebereinstimmung mit der im Text gegebenen Definition eine unendliche Folge  $\alpha_1, \alpha_2, \alpha_3 \dots$  deren jeder Abschnitt eine Gruppe ist, die aber diese Eigenschaft verliert, wenn man für irgend ein  $m$   $\alpha_m$  durch einen umfassenderen Simplex des  $m$ -ten Komplexes ersetzt). Es liegt dann ein höchstens  $n$ -dimensionales approximierendes Spektrum vor (Vgl. ALEXANDROFF, a.a.O., S. 493): höchstens  $n$ -dimensional, weil jeder Simplex infolge von 1) aus höchstens  $n+1$  Elementen besteht; approximierend — mit Rücksicht auf  $(^1)$ . Der durch unser Spektrum "approximierte" Raum ist der im Text definierte Raum  $R^*$ . Mit Hilfe eines URYSOHN'schen Satzes (Vgl. unten Fussnote <sup>18)</sup>) beweist ALEXANDROFF, dass  $R^*$  kompakt, metrisierbar und höchstens  $n$ -dimensional ist.

<sup>13)</sup> Daraus folgt natürlich sofort, dass die Dimension von  $R^*$  genau  $n$  ist.

Verhältnis von allgemeinen Räumen zu den Euklidischen Zahlenräumen. Aus dem Menger'schen Ergebniss, dass jeder ein-dimensionale kompakte Raum mit einer Teilmenge des drei-dimensionalen Euklidischen Raumes homöomorph ist <sup>14)</sup>, folgt bei Heranziehung des hier bewiesenen Theorems, dass (wie dies auch von Menger vermutet wurde <sup>15)</sup>) allgemeiner jeder ein-dimensionale *separable* Raum (insbesondere also jede eindimensionale Teilmenge eines Euklidischen Raumes von beliebiger Dimension) mit einer Teilmenge des Euklidischen  $R_3$  homöomorph ist. Ebenso lässt sich der Menger'sche Fundamentalsatz <sup>16)</sup>, wonach jeder endlichdimensionale kompakte Raum auf eine Teilmenge eines Euklidischen Raumes topologisch abbildbar ist, ohne weiteres auf separable Räume übertragen <sup>17)</sup>.

Eine andere Folgerung ergibt sich aus der folgenden Bemerkung: Die Voraussetzung, dass  $R$   $n$ -dimensional ist, ist in den Beweis unseres Theorems nur durch die Vermittlung der Tatsache eingegangen, dass  $R$  die Behauptung des Satzes I erfüllte. Jeder Raum, welcher dieser letzten Bedingung genügt, ist also mit einer Teilmenge eines höchstens  $n$ -dimensionalen kompakten Raumes homöomorph und a fortiori selbst höchstens  $n$ -dimensional. Es gilt somit neben Satz I auch die Umkehrung:

II. Ist  $n$  eine ganze nicht negative Zahl, —  $R$  ein separabler Raum, und gibt es zu jedem endlichen System  $\mathfrak{C}$  offener Mengen, die  $R$  überdecken, eine Zerlegung von  $R$  in endlich viele abgeschlossene Mengen, deren jede in einer Menge aus  $\mathfrak{C}$  enthalten ist und die zu je  $n+2$  leere Durchschnitte haben, so ist  $R$  höchstens  $n$ -dimensional.

Dieser Satz ist für kompakte Räume mit einem Ergebniss von URYSOHN <sup>18)</sup> äquivalent und ist ebenso wie das letztere zahlreicher Anwendungen fähig.

Das Hauptergebnis dieser Arbeit gestattet eine wesentliche Verallgemeinerung: Es stellt sich heraus, dass man *abzählbar viele* separable Mengen, die in ihrer Summe abgeschlossen sind, *simultan* in kompakte Räume von entsprechenden Dimensionen einbetten kann. Es gilt genau gesprochen:

Seien  $M_1, M_2, M_3 \dots$  abzählbar viele in einem separablen Raum  $R$  gelegene abgeschlossene Mengen. Als topologischer Raum betrachtet, lässt sich dann  $R$  zu einem kompakten metrisierbaren Raum  $R^*$  erweitern,

<sup>14)</sup> Vgl. Menger, diese Proceedings 29, S. 476.

<sup>15)</sup> Vgl. Menger, a.a.O., S. 482.

<sup>16)</sup> Vgl. Menger, a.a.O., S. 482 sowie Jahresbericht d. D. Math.-Ver. 35, S. 149.

<sup>17)</sup> Von Menger wurde dies vermutet. Vgl. Jahresbericht d. D. Math.-Ver. 35, S. 149, Fussnote 4).

<sup>18)</sup> Mit dem Satze nämlich, dass ein kompakter Raum, der für jedes  $\varepsilon > 0$  in endlich viele abgeschlossene Mengen mit Durchmessern  $< \varepsilon$  zerlegbar ist, die zu je  $n+2$  fremd sind, eine Dimension  $\leq n$  besitzt. Vgl. URYSOHN, Fund. Math. 8, S. 294. Dieser Satz ist implicite in den Beweis des Hauptsatzes dieser Arbeit eingegangen, da er die Grundlage für den ALEXANDROFF'schen Satz bildet, auf den wir uns berufen haben (Vgl. Fussnote <sup>12)</sup>).

so dass, wenn  $\overline{M}_n$  die abgeschlossene Hülle von  $M_n$  in  $R^*$  bedeutet, die Dimension von  $\overline{M}_n$  für jedes  $n$  mit der Dimension von  $M_n$  übereinstimmt.

Der Gedankengang des Beweises bleibt in wesentlichen derselbe wie früher. Nur wird an Stelle von Satz I der folgende Satz benützt:

In einem separablen Raum  $R$  sei eine Folge von abgeschlossenen Mengen  $M_1, M_2, M_3 \dots$  gegeben. Zu jeder Zerlegung von  $R$  in endlich viele offene Mengen  $G_1, G_2 \dots G_n$  gibt es dann eine Zerlegung von  $R$  in endlich viele abgeschlossene Mengen  $F_1, F_2, \dots F_q$ , die Teilmengen der  $G_k$  sind, wobei jeder Punkt von  $M_i$  ( $i = 1, 2, \dots$ ) in höchstens  $n_i + 1$  Mengen  $F_k$  liegt, wenn  $n_i$  die Dimension von  $M_i$  bedeutet.

Es entsteht die Frage, ob ein separabler Raum  $R$  stets, in der Weise zu einem kompakten (metrisierbaren) Raume  $R^*$  erweitert werden kann, dass jede in  $R$  abgeschlossene Menge  $M$  ihre Dimension nach der Abschliessung in  $R^*$  bewahrt?

Betrachtet man anstatt der Gesamtdimension des Raumes seine Dimension in den einzelnen Punkten, so gilt das folgende Theorem:

Jeder separable metrisierbare topologische Raum  $R$  ist Teilmenge eines kompakten metrisierbaren Raumes  $R^*$ , so dass in jedem Punkte  $x$  von  $R$  gilt:

$$\dim_x R = \dim_x R^* {}^{19)},$$

(unter  $\dim_x R$ , bzw.  $\dim_x R^*$  die Dimension von  $R$  bzw. von  $R^*$  im Punkte  $x$  verstanden.

Beim Beweise geht man folgendermassen vor: Zuerst zeigt man leicht mit Hilfe des verallgemeinerten BOREL'schen Theorems: Es existiert ein System  $\mathfrak{S}$  von abzählbar vielen in  $R$  offenen Mengen, so dass sich auf jeden Punkt von  $R$  eine Folge von Mengen aus zusammenzieht, deren Begrenzungen (in  $R$ )  $(n(x)-1)$ -dimensional sind, wo  $n(x)$  die Dimension von  $R$  in  $x$  bedeutet. Den Raum  $R^*$  wird jetzt so bestimmt, dass jede beliebige Menge  $U$  aus  $\mathfrak{S}$  Durchschnitt ist von  $R$  mit einer in  $R^*$  offenen Menge  $U^*$ , deren Begrenzung in  $R^*$  mindestens die gleiche Dimension hat, wie die Begrenzung von  $U$  in  $R$ .

Auch an diesen Satz knüpft sich eine Fragestellung an: Bleibt die Behauptung richtig, wenn man verlangt, dass  $R^*$  in allen seinen Punkten (nicht nur in den Punkten von  $R$ ) dieselbe Dimension besitze wie  $R$ ?

<sup>19)</sup> Man kann noch zeigen, dass es einen  $R$  enthaltenden kompakten Raum gibt, der die soeben formulierte Bedingung erfüllt und überdies dieselbe Gesamtdimension besitzt wie  $R$ .



**Physiology.** — *An Experimental Study of the Cerebellar Control of the Vocal Organs.* By LAURETTA BENDER. (Communicated by Prof. G. VAN RIJNBERK and Prof. B. BROUWER).

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## ERRATUM

In Prof. BORTOLOTTI's note, p. 218, lines 9 and 10 from the top to omit:

"two of which (inversely like, corresponding to the two opposite signs of  $\gamma_{ijl}$  or  $T_{\lambda\mu\nu}$ ) are . . ."

and to read:

"each of which — when the connexion is done — is . . ."

